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THE MEASUREMENT OF GOLD AND SILVER BUTTONS IN QUANTITATIVE BLOWPIPE ASSAYS.

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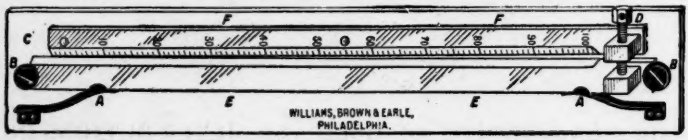
WHEN Harkort, a Freiberg student, invented the quantitative blowpipe assay for gold and silver, in 1824, he was at once confronted with the impossibility of weighing the very small buttons obtained. He surmounted the difficulty by assaying a silver ore repeatedly in the muffle, until he knew with exactness its contents. Then he assayed a standard weight of it by the blowpipe and obtained a button of a certain size whose weight was known from the amount of ore taken. Taking half and a third and a quarter of the weight of ore he obtained smaller buttons of known weight. With these he constructed a scale. He drew two fine slightly diverging lines on white cardboard, placed the buttons between the lines at the points where they fitted, and marked opposite those points the corresponding weights, or, rather, the corresponding silver contents of the ore, assuming a standard weight taken for assay.

Harkort brought the method to the attention of Plattner, the professor of metallurgy at Freiberg, and published his results at his own expense in a small book entitled "Silverprobe vor dem Löthrohr," Freiberg, 1827.

Plattner took up this method in his regular course of instruction, and improved and extended it. One of his principal improvements was the construction of the button scale ruled on ivory, made by the mechanic, August Lingke, at Freiberg. To fix accurately the dimensions of this scale, Plattner assayed a very rich silver ore repeatedly in the muffle until it was known with certainty to contain exactly 3.48 per cent. of silver. He then made repeated blowpipe assays of this ore, obtaining buttons very close together in size and weight. The two lines were then drawn on ivory so that they diverged approximately the diameter of these buttons in 150 millimeters. The buttons were then fitted exactly between the lines, and the point marked 50, the



distance from here to the meeting point of the lines being divided into fifty equal divisions. The exact dimensions of the scale as thus made were 156 mm. from 0 to 50, and the lines 0.9 mm. apart at 50. The weights corresponding to the various numbers were calculated from the number 50 representing 3.48 milligrams of silver (when 100 mg. were taken for analysis), using the assumption that as the buttons were nearly spheres, or, at least, were homologous in shape, their weights would vary as the cubes of their respective horizontal diameters. The weight of the silver button corresponding to any number from 1 to 50 would be therefore $3.48 \times \left(\frac{n}{50}\right)^3$, and thus these weights were all calculated and engraved on the scale opposite the numbers. A similar set of weights was obtained in an exactly similar manner for gold buttons. Thus the Plattner ivory scale was devised and is still used more extensively than any other method of measuring these small buttons.

The defects of the Plattner scale may be enumerated under the heads of:

1. Errors in construction.
2. Errors in using.

The errors in constructing the scale may be as follows:

a. The lines are sometimes not mathematically straight.

b. The lines may be rough or ragged.

c. The lines may not meet exactly at the point marked zero.

d. The lines may not be exactly the right distance apart (0.9 mm.) at the point marked 50.

It is seldom that the best scales made in Freiberg are free from one or more of these defects; I do not believe that more than one out of five is perfect.

The errors in using the scale consist of:

a. Placing the button too high or too low through optical illusion. The button should be tangent to the inside of the lines, and in a strong light the white metallic surface of the button is difficult to see on its outer edge. One investigator has even proposed putting the silver buttons a short time into ammonium sulphide, so as to blacken them and thus facilitate their measurement.

b. Placing the button too high by virtue of parallax, which projects the middle diameter of the button against the scale on which it rests, and makes the button seem to fit higher up than its real diameter. The remedy for this is to sight first down one side of the button, then down the other, each time looking perpendicularly to the scale. This operation is tedious, and takes considerable experience.

c. The button being nearly round, it takes considerable time, patience, and experience to get it to a certain spot on a flat surface. This is not an error of the scale, but an unavoidable inconvenience, which becomes accentuated if the ivory warps, so that the scale does not lie level. A beginner will frequently make a greater mistake in measuring a button than in getting it.

Goldschmidt's Method.—Dr. V. Goldschmidt, of Heidelberg, proposed two improvements:

1. *To Remelt the Cupelled Buttons on Charcoal.*—This gives to them a more nearly spherical and more uniform shape than is obtained on the cupel. The button is to be removed from the cupel, hammered flat between paper, to clean it, and then touched with the reducing flame, on charcoal, just long enough for it to melt and take the spherical form. Buttons thus remelted will be heavier than cupelled buttons of the same horizontal diameter, and, therefore, heavier than the given weights on the Plattner scale.

2. Measuring the Horizontal Diameter of Such Remelted Buttons Under the Microscope.—For this purpose, a divided scale is put into the focus of the eyepiece of a compound microscope magnifying 50 to 100 diameters. A scale of 40 divisions is very suitable, the tenths of each division being estimated when measuring. The buttons are placed on a glass plate, a piece of blue glass gives a nice background, and since they come to rest only on their bases, the horizontal diameter is always in position to be measured. The diameter being known in whole divisions and tenths, reference to a previously constructed table gives the volume and weight of the button, when of gold or silver.

To construct this table, the following ingeniously devised plan was worked out by Goldschmidt: A number of bits of pure gold are melted on charcoal. The buttons obtained are each measured separately, in divisions on the scale. All the buttons are then weighed together, as accurately as possible. The total weight, divided by the specific gravity of gold, gives the sum of the volumes of the buttons. This latter, divided by the sum of the cubes of the separate diameters (expressed in divisions on the scale), gives a function μ. This function is the factor by which to multiply the cube of the diameter of any button to get its individual volume. Expressed algebraically, the above operations are:

$$\frac{\Sigma \text{ weight}}{\text{Sp. gr. gold}} = \Sigma \text{ volumes.}$$

$$\frac{\Sigma \text{ volumes}}{\Sigma \text{ (diam.)}^3} = \text{a function} = \mu.$$

Volume of any button $= \mu \times (\text{diam.})^3$

Weight of a gold button $= \mu \times$ sp. gr. gold $\times (\text{diam.})^3$

Weight of a silver button $= \mu \times$ sp. gr. silver $\times (\text{diam.})^3$

From the above data, a table can be constructed showing the weights of gold or silver buttons for every division of the scale up to its full range.

It should be remembered that measurement under the microscope is a very satisfactory laboratory method, but as it requires a compound microscope, it is not suitable for field use or prospector's outfits.

Richards' Scale.—The writer adopts Goldschmidt's idea of remelting the button on charcoal, wherever practicable, but has

devised a modification of Harkort's method for measuring the buttons.

The idea is to make two metallic edges perfectly straight, lying on a flat surface, touching each other at one point and held apart at the other extremity by a set-screw, so that the point 100 may indicate a fixed width or separation of almost exactly one millimeter. In reality, the button whose horizontal diameter fits at 100 has a diameter of 1.02 millimeters, but this distance has been so chosen that the volume and consequently the weight of said button are exactly that of a perfect sphere whose diameter is one millimeter. The other numbers on the scale have the same significance; for example, the button whose horizontal diameter fits at 43.5 has the volume and weight of a sphere whose diameter is 43.5 hundredths of a millimeter, and such is the basis on which the table is calculated.

In using the scale, the button is put into the groove, the scale inclined slightly and tapped until the button wedges itself. The tenths of a division are estimated, taking the points where the sides of the button touch the scale as the reading. As the button may sometimes roll with its shorter vertical diameter across the scale, several readings are taken, and the highest reading occurring with regularity is the true horizontal diameter. For instance, among 43.4, 43.4, 41.6, 43.5, 41.8, 43.5, it is evident that 43.5 is the horizontal diameter and 41.6 or 41.8 the vertical. The button can also be observed under the lens, to see how it is lying, at any given reading.

A gentle spring keeps the right-hand strip against the set screw, thus allowing it to be pressed back for cleaning out the slot with a brush or removing a button. The scale is made of hardened aluminum, for lightness, and is set in a velvet-lined leather case. It is made by Williams, Brown, and Earle, of Philadelphia, and sold at the same price as the imported ivory Plattner scales. P. Stoë, of Heidelberg, makes and sells the scales in Germany.

The advantages of this method of construction over the engraved ivory scale are:

1. The edges are perfectly straight, from the method of construction.

2. They meet exactly at the zero point and can be adjusted to the exact distance at 100.

3. The reading is more or less automatic, the errors of placing, parallax, and personal equation being almost entirely eliminated.

The scales are adjusted by the makers, but, if by accident they get out of adjustment, a small rod of wire furnished with each instrument, whose lower end marks a given reading on a correct instrument, provides the means of quick readjustment.

Measuring Gold-Silver Alloy Buttons.—When the button obtained is pure gold or pure silver, any of the above methods give its weight directly. If, however, it is an alloy of the two, and is too small to weigh satisfactorily, but must be measured, the question of determining the silver present as well as the gold is a difficult one. The determination is very much facilitated by using the small case of standard alloys designed by Dr. Goldschmidt, of Heidelberg (made by P. Stoë, Heidelberg, imported by Williams, Brown, and Earle, Philadelphia). This is a small tablet in a brass case, containing small flattened buttons of gold-silver alloys, every 1 per cent. of silver to 20, then every 2 per cent. to 40, and every 4 per cent. to 56, where the alloy becomes silver-white. In using, the alloy button to be tested is hammered flat between paper, put on the plate and examined under the lens by diffused daylight. With a little experience, the button can be placed to one alloy. The observation gives the per cent. of silver in the button. Assayers working by the muffle will also find this a very convenient instrument to save parting where a quick, approximate determination is wanted, or to determine how much silver to add to an alloy to get the right proportions for nitric acid parting.

I have classified the different methods available to the blowpipe assayer as follows:

I. If the button is over 50 per cent. of gold, and therefore colored, melt on charcoal, measure, and note its *volume*. Then proceed by either of the following methods:

(*a*) Flatten out, compare with the standard alloys, and get the per cent. of silver in it. From the table of specific gravities of gold-silver alloys take the specific gravity. Multiply the *volume* of the alloy by its specific gravity; the product is its weight. From the known percentage of silver and gold in it, calculate their respective weights.

(*b*) Melt the button with a button of pure silver having an equal diameter, if the color of the alloy is pale; or of 25 per

cent. greater diameter, if the color is brass-yellow; or of 50 per cent. greater diameter, if of nearly pure gold color. Hammer out flat, and part with nitric acid in the usual way. Wrap the gold in a small piece of pure lead foil, cupel, remelt, measure, and thus get its weight and note its volume. Subtract the volume of the gold from the volume of the alloy, and the difference is the volume of the silver. The weight of silver corresponding to this volume is obtained directly from the table.

The writer has verified these two methods of procedure, and found them both reliable. The principle of method (*a*) is due to V. Goldschmidt, but not exactly in the simple form given above. The principle of method (*b*) is based on the fact that gold and silver neither contract nor expand in alloying, which fact the writer has verified by experiment and calculation.

II. If the button is less than 50 per cent. gold, and, therefore, silver colored. Melt on charcoal and note its *volume*. Then proceed by either:

(*a*) Part with nitric acid (remelting with more silver if not attacked). Wrap the gold in lead foil, cupel, remelt, measure, note its weight and volume. Subtract its volume from that of the alloy, getting the volume of the silver, and thence its weight.

(*b*) Measure accurately a pure gold button of approximately the same diameter as the alloy button. Melt together on charcoal, and measure carefully, noting the *volume*. Flatten out the color will be yellow), compare with the standard alloys, and, knowing the volume, compute the weight of gold and silver present. The weight of gold found less the weight of the gold button added, gives the weight of gold in the original assay button. The weight of silver may be obtained by calculation from either the original alloy button or the yellow one after gold had been added.

This method of procedure was suggested by Professor B. W. Frazier, of Lehigh University.

(*c*) Replace on charcoal, and heat intensely in the point of the oxidizing flame. The silver slowly volatilizes, and in one to five minutes the alloy becomes yellowish. It is difficult to drive all the silver off, as the last five or ten per cent. volatilize slowly and probably also take a little gold with them. It is best to stop when the alloy has a pronounced yellow color, measure, note the volume, flatten out, compare with standard alloys, and calculate

the weight of gold present. Take the volume of that weight of gold from the table, subtract from the volume of original alloy button, and thus obtain the volume and thence the weight of the silver.

The fact that silver can be volatilized from gold in this way, on charcoal, was described by the writer in the *Journal of the Franklin Institute*, June, 1896.

The writer finds methods I (*a*) and II (*c*) the most suitable for field work; the parting with nitric acid is preferably a laboratory method, and is the most accurate.

Note on the Quantitative Gold or Silver Assay.—The writer makes the fusion on charcoal in preference to a Freiberg carbon crucible, which is often unobtainable. When finished, it is always possible to make the slag quite liquid and then to pour out the lead *in toto*, leaving only clean slag on the charcoal. At first, it will be best to pour out on a cold steel anvil or plate, whence the lead may be picked up and placed at once on the cupel for scorifying. The writer has frequently poured the lead directly from the charcoal on the previously heated cupel, and then commenced immediately to scorify, sometimes without even allowing the lead to set. This will usually succeed for one with a steady hand, and several minutes can thus be saved.

In scorifying, if the blowpipe-tip is advanced almost to the nearer edge of the flame, an oxidizing flame of great power without a well-defined point is obtained, before which the lead oxidizes with great rapidity. 1800 mg. of lead were thus scorified to 300 mg. in two minutes; and, in general,one-half to two-thirds of the time usually consumed in scorification can be saved.

For fine cupellation, it is not absolutely necessary to pre-heat the cupel. The button is placed on the freshly struck cupel, a spot under the button strongly heated, on which the button drops as its melts. Then the cupel is turned slowly, keeping the button half-way up the far side, and the flame always heating the cupel just under it, which is thus dried before the button comes onto it.

By using such devices as the above to save time, the gold or silver assay may often be run through in from ten to fifteen minutes, with an extra five minutes for separately determining gold and silver, if necessary.

Number on the scale.	Weight of gold button.	Weight of silver button.	Volume of the button.	Number on the scale.	Weight of gold button.	Weight of silver button.	Volume of the button.
1ooths mm.	mg.	mg.	cu. mm.	1ooths mm.	mg.	mg.	cu. mm.
2	0.0001	0.00004	0.000004	42	0.747	0.406	0.0388
3	0.0003	0.00015	0.000014	43	0.802	0.436	0.0416
4	0.0006	0.00035	0.000034	44	0.859	0.467	0.0446
5	0.0013	0.00069	0.000065	45	0.919	0.500	0.0477
6	0.0022	0.0012	0.00011	46	0.982	0.534	0.0510
7	0.0035	0.0019	0.00018	47	1.047	0.569	0.0544
8	0.0052	0.0028	0.00027	48	1.115	0.606	0.0579
9	0.0074	0.0040	0.00038	49	1.186	0.645	0.0616
10	0.0101	0.0055	0.00052	50	1.261	0.686	0.0655
11	0.0134	0.0073	0.00070	51	1.338	0.727	0.0695
12	0.0174	0.0095	0.00091	52	1.418	0.771	0.0736
13	0.0222	0.0121	0.00115	53	1.501	0.816	0.0780
14	0.0277	0.0151	0.00144	54	1.588	0.863	0.0824
15	0.0340	0.0185	0.00177	55	1.678	0.912	0.0871
16	0.0413	0.0225	0.00214	65	1.771	0.963	0.0920
17	0.0495	0.0269	0.00257	57	1.867	1.016	0.0970
18	0.0588	0.0320	0.00305	58	1.967	1.070	0.1022
19	0.0692	0.0376	0.00359	59	2.07	1.126	0.1075
20	0.0807	0.0439	0.00419	60	2.18	1.185	0.1131
21	0.0934	0.0508	0.00485	61	2.29	1.245	0.1189
22	0.107	0.0584	0.00558	62	2.40	1.307	0.1248
23	0.123	0.0667	0.00637	63	2.52	1.371	0.1309
24	0.139	0.0758	0.00724	64	2.64	1.438	0.1373
25	0.158	0.0857	0.00818	65	2.77	1.506	0.1438
26	0.177	0.0963	0.00920	66	2.90	1.577	0.1505
27	0.199	0.108	0.0103	67	3.03	1 649	0.1575
28	0.221	0.120	0.0115	68	3.17	1.724	0.1646
29	0.246	0.134	0.0128	69	3.31	1.802	0.1720
30	0.272	0.148	0.0141	70	3.46	1.881	0.1796
31	0.300	0.163	0.0156	71	3.61	1.963	0.1874
32	0.330	0.180	0.0172	72	3.76	2.047	0.1954
33	0.362	0.197	0.0188	73	3.92	2.133	0.2037
34	0.396	0.216	0.0206	74	4.09	2.222	0.2122
35	0.432	0.235	0.0225	75	4.25	2.313	0.2209
36	0.470	0.256	0.0244	76	4.43	2.407	0.2298
37	0.511	0.278	0.0265	77	4.60	2.504	0.2390
38	0.553	0.301	0.0287	78	4.78	2.602	0.2485
39	0.598	0.325	0.0311	79	4.97	2.704	0.2582
40	0.645	0.351	0.0335	80	5.16	2.81	0.268
41	0.695	0.378	0.0361	81	5.36	2.91	0.278

Number on the scale.	Weight of gold button.	Weight of silver button.	Volume of the button.	Number on the scale.	Weight of gold button.	Weight of silver button.	Volume of the button.
100ths mm.	mg.	mg.	cu. mm.	100ths. mm.	mg.	mg.	cu. mm.
82	5.56	3.02	0.289	92	7.85	4.27	0.408
83	5.77	3.14	0.299	93	8.11	4.41	0.421
84	5.98	3.25	0.310	94	8.38	4.55	0.435
85	6.19	3.37	0.322	95	8.65	4.70	0.449
86	6.41	3.49	0.333	96	8.92	4.85	0.463
87	6.64	3.61	0.345	97	9.20	5.00	0.478
88	6.87	3.74	0.357	98	9.49	5.16	0.493
89	7.11	3.87	0.369	99	9.78	5.32	0.508
90	7.35	4.00	0.382	100	10.08	5.48	0.524
91	7.60	4.13	0.395				

SPECIFIC GRAVITY OF GOLD-SILVER ALLOYS.

Silver. Per cent.	Specific gravity.	Silver. Per cent.	Specific gravity.	Silver. Per cent.	Specific gravity.
0	19.258	34	14.984	68	12.263
1	19.099	35	14.887	69	12.198
2	18.940	36	14.791	70	12.133
3	18.785	37	14.697	71	12.069
4	18.632	38	14.603	72	12.007
5	18.483	39	14.511	73	11.944
6	18.335	40	14.420	74	11.882
7	18.190	41	14.330	75	11.821
8	18.047	42	14.241	76	11.761
9	17.906	43	14.153	77	11.700
10	17.767	44	14.066	78	11.641
11	17.631	45	13.980	79	11.582
12	17.497	46	13.896	80	11.525
13	17.364	47	13.813	81	11.467
14	17.234	48	13.730	82	11.410
15	17.106	49	13.648	83	11.353
16	16.979	50	13.568	84	11.297
17	16.855	51	13.488	85	11.242
18	16.731	52	13.409	86	11.187
19	16.610	53	13.331	87	11.133
20	16.491	54	13.254	88	11.079
21	16.374	55	13.178	89	11.026
22	16.258	56	13.103	90	10.973
23	16.144	57	13.029	91	10.921
24	16.031	58	12.955	92	10.871
25	15.920	59	12.882	93	10.819
26	15.810	60	12.811	94	10.768
27	15.702	61	12.739	95	10.718
28	15 595	62	12.669	96	10.618
29	15.490	63	12.600	97	10.619
30	15.386	64	12.531	98	10.570
31	15.283	65	12.463	99	10.521
32	15.183	66	12.395	100	10.473
33	15.083	67	12.329		

BLOWPIPE LABORATORY, LEHIGH UNIVERSITY,
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NOTES ON SOME BLOWPIPE TESTS.

By Joseph W. Richards.

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Closed Tube Test.—This test may easily be made quantitative for approximate determinations of water, volatile sulphur, etc. A weighed amount of material is put into the tube, tapped down, and heated regularly. The upper part of the tube containing the sublimate is then nicked with a file and broken off. If water is being determined, two small corks are put into its ends, to prevent evaporation. The piece of tube and sublimate are then weighed; then the tube is heated until the sublimate is driven off, and weighed again. The results on pyritic ores have proved satisfactory. A piece of göthite gave 10.28 per cent. water; theory requires 10.11 per cent. Time, five minutes.

Open Tube Test.—The behavior of the antimony coat is sometimes different from that usually described in the books. The entirely volatile oxide, Sb_2O_3, is sometimes the only product, not a trace of the non-volatile Sb_2O_4 being formed. I have observed this in allemontite, dyscrasite, and ullmannite, particularly. It takes nearly a red heat to volatilize this coating, and if the upper end of the tube from which the vapors are escaping be held in the flame, the latter is colored pale yellowish green (arsenic, pale blue). Penfield is the only writer who mentions the formation of this volatile coating exclusively by some minerals, but his experience as to which give it does not exactly coincide with mine.

It is important when testing in the open tube, if any substance whatever does not give a sublimate in lump, to powder it, and finally to heat with the blowpipe flame from the outside as hot as the glass will stand. Some sulphides, such as sphalerite and argentite, do not roast until thus heated. With these precautions, the test is uniformly reliable.

Flame Tests.—When testing for phosphoric acid, the assay on platinum wire is touched when *hot* to concentrated sulphuric acid, and brought into the outside edge of the Bunsen flame as *low down* as possible, and as slowly as possible. By thus proceeding, phosphorus can be infallibly detected in any combination, according to my experience, thus rendering unnecessary the ammonium molybdate test. The flame is slightly bluish green close to the

wire, grayish green a short distance away, and yellowish green farther off.

When testing similarly for boron, the assay should be held slightly higher, say an inch higher, in a hotter part of the flame. When testing for boron with Turner's mixture, it is an advantage to moisten the mass to a paste with a drop of concentrated sulphuric acid, and then put moist into the edge of the flame.

Reduction to Metal.—When reducing with soda on charcoal, if an assay proves very refractory, it is uniformly of advantage, and never deleterious, to add some borax to the assay. This is particularly useful in reducing tin oxide, and is to be preferred to potassium cyanide because of its harmlessness.

Test for Fluorine.—The fusion with potassium bisulphate decomposes any fluoride, but the test of the vapors with Brazil wood paper is not reliable. Light, air, and age, seem to deteriorate rapidly the sensitiveness of the paper. I have found it more reliable to make the fusion in a rather large closed tube, of say 5 to 8 mm. diameter, heating regularly with the tube almost horizontal. The silica ring deposits just above the assay, and the odor of the gas is often quite plain. Cool the tube, nick it below the silica ring, break, and hold the upper end vertically under, and close to the nose. At this instant the odor of hydrofluoric acid will be perceived with certainty, if any has been driven off, and by a little experience the odor can be distinguished with as much certainty as the smell of ammonia. A still more conclusive proof consists in letting water run slowly over the silica ring. If it is merely a sublimate of a volatile salt, it will be dissolved and disappear; if it is the true silica ring, it will become gelatinous, seen under the lens, and on carefully drying the tube the white ring is again strongly in evidence.

Test for Arsenates.—All give the arsenic odor and coat on charcoal, but sometimes so slowly as easily to escape detection. Mixing with charcoal dust and soda, and fusing in the closed tube or open tube does not invariably give metallic arsenic or the oxide, on account of the heat being insufficient to reduce some arsenates, *e. g.*, of zinc. Putting this mixture in the lower end of an open tube, and playing on it with the reducing flame of the blowpipe directed into the tube, will always give the arsenic coating. All mercury compounds are also thus reduced, and deposit a mercury coating, and it is a good means of testing for antimonates, tellu-

rates and selenates, while ammonium compounds give ammonia gas.

Test for Silica in the S. Ph. Bead.—Many silicates are attacked rapidly, the bases dissolved, and the silica left either in flocks or as a skeleton. However, on long blowing, some silica dissolves in the bead, and if only a small piece of mineral is used and the blowing is strong, all may dissolve up clear. Hirschwald determined that the bead can dissolve 2.5 per cent. of its weight of silica; my tests have shown close to 2 per cent. but that more can be dissolved if other bases are present. For instance, the bead dissolves—

2.25 per cent. of silica if no other base is present,
2.25 " " " " 3.85 per cent. of alumina is present,
3.03 " " " " 8.52 " " lime " "
3.40 " " " " 3.17 " " " " "
4.04 " " " " 10.91 " " zinc oxide is present.

It results from this behavior, that in silicates rich in bases, an amount of mineral equal to even 30 per cent. of the weight of the bead (as in thaumasite) may be dissolved up clear. Two observations will obviate this difficulty. If the mineral is not white, as it is attacked, the edges will become white and clear as it is being dissolved, and the presence of silica thus proved. If the piece is white or clear, the blowing must be interrupted several times, and then with the lens the silica can be recognized floating in the bead. If the bead is clear, a further addition of a lump, say one-third the size of the bead, will always, on further blowing, cause the opalescent milkiness due to silica. By attending to these points, I think that silica can be found with certainty in all these silicates which are easily decomposed.

A different case is presented by those silicates which are attacked slowly and dissolve *en masse*, without showing a skeleton. They are not numerous, and are principally the silicates of aluminum, glucinum, or zirconium. In such cases, by long blowing (five minutes), enough silica is usually dissolved in a small bead to make it milky opalescent, which silica alone produces when present in such a small amount as even less than three per cent. The presence of silica can thus be proved. The minerals which dissolve slowly in salt of phosphorus and do not contain silica are principally corundum, diaspore, chrysoberyl, cassiterite, spinel, chromite, gahnite, and xenotime. They should be brought to mind and kept in consideration in connection with such few silicates as dissolve very slowly like the above.

BLOWPIPE LABORATORY, LEHIGH UNIVERSITY,
January 17, 1901.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

NOTES ON SUGAR BEETS.

BY P. F. TROWBRIDGE.

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OBTAINING THE TARE.

AT the different beet-sugar factories in Michigan, two methods are used for finding the amount of tare (dirt adhering to the beets).

1. A half bushel of beets is taken from each wagon or car, as a sample, satisfactory to both the farmer and the factory representative. From this sample 20 or 25 pounds are carefully weighed. These beets are then well brushed with bristle brushes, and retopped if the whole of the crown has not been removed. The beets are again weighed and the loss in weight computed to per cent. is reported as the amount of tare.

2. The weighed sample is washed in a revolving washer, allowed to drain for a few minutes, retopped if necessary and again weighed. The loss in weight is reported in terms per cent. The second method requires less labor and is more rapid. It is also more nearly in accord with the factory operation. The first method fails to remove every particle of dirt, but does remove many small rootlets and a small amount of the outside of the beets, especially if they have been frozen.

In method 2, the adherent water tends to decrease the amount of tare. In the following series of experiments made at one of the Michigan factories, care was exercised to make both samples from each load as representative as possible.

No. of sample.	Tare by method 1. Per cent.	Tare by method 2. Per cent.	Difference.
1	8.75	6.25	+2.50
2	10.00	8.75	+1.25
3	13.75	13.75	0.00
4	7.50	7.50	0.00
5	5.00	6.25	—1.25
6	21.25	22.50	—1.25
7	8.75	6.25	+2.50
8	10.00	7.50	+2.50
9	11.25	11.25	0.00
Average	10.14	10.00	+0.14

A further advantage of the second method is that frozen beets may be tared at once using warm water in the washer.

ANALYSIS OF THE SAMPLE.

The percentage of sugar in the beet is determined, in all the Michigan factories, by the indirect method of juice analysis, using a factor to express the results in terms of per cent. in the beets. A brief résumé of the methods employed may be of interest.

A portion of the tared sample (usually longitudinal quarters of six or eight beets) is pulped in a revolving grater. The pulped sample is mixed, pressed in a lever press, and the juice sent to the chemist for analysis. Factory methods vary somewhat at this point: (1) The sample is allowed to stand for fifteen or twenty minutes to allow the air bubbles to escape, after which the Brix reading is taken with correction for temperature; then 100 cc. of the sample are poured into a double graduated flask (100–110 cc.), and 10 cc. of basic lead acetate solution added. If foam renders filling to the mark difficult, a drop of ether or alcohol is used. The sample is thoroughly mixed, filtered through a dry filter and polarized. The per cent. of sugar in the juice is given in Schmitz's tables, and the factor adopted by the factory is used to express the results in terms of per cent. sugar in the beet. (2) After the Brix reading a double normal sample (52.1 grams) is measured with a sucrose pipette, which has a graduation on the stem indicating the amount to be taken for the different degrees Brix. The pipettes have been graduated with a pure sugar solution, and are not strictly accurate for beet juices, but the error is well within the range allowed by commercial methods. The sample is transferred to a graduated flask, 100 or 200 cc., 6 or 8 cc. of lead acetate solution added, the flask filled to the mark, and the sample mixed, filtered, and polarized. If 100 cc. flasks are used, one-half the reading gives the per cent. sugar in juice, and the factor gives per cent. in beet. (3) A double normal sample of the juice is weighed on a balance sensitive to 10 mg.; then proceed as in (2). All the methods give results, the commercial accuracy of which cannot be questioned. Method (1) by employing a larger sample reduces the errors of manipulation and reading, and is thus preferred by the writer.

THE FACTOR TO SHOW THE RELATION BETWEEN SUGAR IN JUICE TO SUGAR IN BEET.

The true factor to represent the relation of sugar in juice to

sugar in beet has been the subject of some controversy and hard feeling between the farmers and the factory managers. During the campaign of a year ago some of the Michigan factories used the factor 0.95, others as low a factor as 0.90, and it was claimed that one factory used a factor of 0.87. The factor 0.95 was formerly employed by the German chemists and was based on the fact that the marc in the beet is usually not far from 5 per cent. Scheibler's method of direct beet analysis showed the error of this assumption, and has brought about the abandonment of this factor on the continent.[1] During the fall and winter of 1899 the writer made a series of twenty-five analyses (method of operation given below) to determine this factor and found as an average 0.919, with a maximum of 0.956, and a minimum of 0.875. The table of results as given below is arranged not in order of the analyses but in order of the value of the factor.

No. of sample.	Sugar in juice. Per cent.	Sugar in beet. Per cent.	Factor.
1	14.6	12.8	0.875
2	15.4	13.6	0.880
3	15.1	13.3	0.881
4	16.0	14.2	0.888
5	15.2	13.5	0.888
6	14.1	12.7	0.899
7	14.8	13.6	0.902
8	15.5	14.0	0.903
9	16.9	15.4	0.911
10	15.3	14.0	0.915
11	15.3	14.0	0.915
12	14.4	13.2	0.917
13	16.8	15.4	0.917
14	16.8	15.4	0.917
15	16.7	15.4	0.922
16	15.7	14.5	0.924
17	15.1	14.0	0.927
18	15.6	14.5	0.929
19	15.1	14.1	0.934
20	11.4	10.7	0.938
21	15.3	14.4	0.941
22	15.7	15.0	0.955
23	15.4	14.7	0.955
24	15.8	15.1	0.956
25	15.8	15.1	0.956
Average	15.4	14.1	0.919

[1] Stohmann: "*Zucker Fabrikation*," (1900), 4te Aufl., p. 52.

METHOD OF ANALYSIS IN DETERMINING FACTOR.

The finely pulped samples are well mixed and duplicate samples are weighed for determination of sugar in beet by the hot alcohol digestion method. The remainder of the pulp is pressed in a lever press, and the juice analyzed by the methods previously described. The samples of pulp, 52.1 grams, are transferred to a 201.2 cc. flask, 6 to 8 cc. of basic lead acetate solution are added, and the flask is then filled three-fourths full of 90 per cent. alcohol. After the flask is fitted with a condenser tube it is heated, immersed in a water-bath, for thirty minutes. Care must be taken that the alcohol does not boil so violently as to force the pulp and juice into the condenser tube. The condenser tube and the neck of the flask are then rinsed with alcohol, and the flask filled nearly to the mark, the flask being turned from side to side to insure the removal of all air bubbles. The flask is then returned to the water-bath for three or four minutes, or until the alcohol is heated nearly to boiling. The contents of the flask are then cooled to about 17.5°. The flask is filled to the mark, thoroughly shaken, and the contents filtered through a dry filter, and polarized. In the filtering, the funnel must be covered to prevent evaporation of the alcohol, and the temperature of the room must be as nearly 17.5° as possible.[1] The reading of the polariscope gives the per cent. of sugar in the beet direct. The sugar in the juice divided by the sugar in the beet gives the factor.

During the campaign of a year ago, shortly after the writer had made the analyses reported above, Mr. E. E. Ewell, first assistant chemist of the Department of Agriculture, was called into the state to examine the working of one of the beet-sugar factories, and made eight analyses to determine the factor. He reported[2] an average factor of 0.9275, maximum 0.945, minimum 0.902.

During the present campaign the Holland Sugar Co., of Holland, Michigan, saves a handful of pulp from every sample analyzed, and for every ten samples this pulp is mixed and analyzed by hot water digestion. This establishes a factor for every ten samples. During three weeks in October they reported to the writer the finding of average factors of 0.91, 0.913, and 0.912.

The writer has made a number of analyses of beets grown the past season in a further study of this problem, with the following

[1] See Wiley: This Journal, **21**, 568 (1899).

[2] House Document, No. 699, p. 146.

results: Average factor 0.917, minimum 0.883, maximum 0.955.

Number.	Purity.	Sugar in juice. Per cent.	Sugar in beet. Per cent.	Factor.
1	81.4	13.6	12.2	0.897
2	80.2	13.5	12.5	0.926
3	78.2	13.4	12.8	0.955
4	80.4	11.5	10.4	0.904
5	78.0	12.5	11.7	0.936
6	83.1	13.0	11.6	0.892
7	84.7	15.0	13.8	0.920
8	84.5	14.6	12.9	0.883
9	77.7	11.0	10.1	0.918
10	77.1	11.1	10.4	0.937
Average	80.5	12.9	11.8	0.917

Mr. Ewell,[1] in his report, calls attention to reasons why there should be so great variations in the relation existing between the sugar in the juice and that in the beet as a whole. It is quite evident that the *average* factor expressing this relation lies between 0.91 and 0.92. If any one grower of beets has a large number of loads to deliver and thus obtains the average of many analyses the use of an average factor will not work injustice to either party. On the other hand the average of a few samples only, may work an injustice to the grower or to the factory.

Owing to the great number of analyses made daily at the factories (100 to 300), the chemists are forced to use the indirect method of juice analysis. The hot alcohol digestion method is too slow and also too expensive. The hot water digestion method, although more rapid than the hot alcohol digestion, is yet too slow for factory use under present factory conveniences. The instantaneous diffusion method of Pellet[2] can be made rapid enough for factory work, but so far as I am aware, it has not yet superseded the indirect method in any of the sugar factories in this country. Difficulty is experienced in pulping the beets sufficiently fine to insure accuracy of results. Theoretically every cell wall should be broken. The sugar does not diffuse through the cell walls with cold water until after the cell walls have been heated.[3]

THE MARC AND THE FACTOR.

It has been shown that the old factor 0.95, based on the approximate 5 per cent. of marc, has no justification. A few actual

[1] *Loc. cit.*

[2] Spencer: "Handbook for Beet-Sugar Chemists," p. 181 (1897).

[3] Stohman: *Loc. cit.*, p. 110.

determinations of marc and factor in the same sample will be of interest. The marc (insoluble fiber) determinations were made as directed by Fruehling and Schulz.[1]

Number.	Marc. Per cent.	Sugar in juice. Per cent.	Sugar in beet. Per cent.	Factor.	Factor on basis of marc.
1	4.47	13.58	12.17	0.896	0.9553
2	4.53	13.48	12.53	0.930	0.9547
3	4.14	11.43	10.66	0.933	0.9586
4[2]	5.20	14.4	11.3	0.785	0.9480
5[3]	4.42	14.2	10.3	0.725	0.9558

VARIATIONS OF SUGAR CONTENT IN BEETS GROWN UNDER APPARENTLY UNIFORM CONDITIONS.

Complaint has been made at different factories in the state that two loads of beets drawn from the same field, and often from the same pit, would vary several per cent. in sugar content. At Marine City this year an average sugar content for about 60 acres of beets for one man was 14 per cent., yet from the same field one load gave 11.8 per cent. and another 18 per cent. This variation is in part due to the variable factor as discussed in the section above, and also in the variation in the sugar content in beets grown under apparently uniform conditions.

The writer raised a small patch of beets last season, about 25 by 50 feet, planting them in rows 16 inches apart, and thinning to about 9 inches in the row. From the patch 120 beets were selected that were of good form and size. Each of these beets were analyzed separately for sugar content some six weeks after they had been pulled. The average sugar content was 12.61 per cent; the lowest was 8.7 per cent., and the highest 18.2 per cent.

Of these 120 beets:

1	beet	contained	between	8	and	9	per cent.	sugar (8.7).
1	"	"	"	9	"	10	"	"
14	"	"	"	10	"	11	"	"
22	"	"	"	11	"	12	"	"
39	"	"	"	12	"	13	"	"
19	"	"	"	13	"	14	"	"
18	"	"	"	14	"	15	"	"
4	"	"	"	15	"	16	"	"
1	"	"	"	16	"	17	"	"
0	"	"	"	17	"	18	"	"
1	"	"	"	18	"	19	"	" (18.2).

[1] "Anleitung," 5th edition, p. 185.

[2] Sample No. 4 consisted of a very large hollow beet, but not decayed.

[3] Sample No. 5 consisted of three green beets.

It is surprising that beets grown under apparently uniform conditions of soil and culture should show such a range of sugar content. The variation of sugar content in individual beets shows the necessity of taking similar portions of several beets for the sample rather than the whole of one or two beets.

The purity (percentage of sugar in total solids) in ten samples from the same patch of beets averaged 80.5 per cent. and ranged from 77.1 to 84.7, as shown in the table on page 220.

COMPARISON OF ANALYSES BY DIGESTION WITH HOT ALCOHOL AND HOT WATER.

The German chemists have adopted the digestion with hot alcohol as the standard, while the French chemists rely upon the digestion with hot water. It will be of interest to compare the results of the two methods. The samples of beets were all grated on a hand vegetable grater, thoroughly mixed, and double normal samples weighed for analysis. The time of digestion was one-half hour in all cases. The general plan of manipulation as given in Fruehling and Schulz[1] was followed. Duplicate samples were taken in every case, three readings being made for each sample. The per cent. reported in the following table is the average of the six readings.

No. of sample.	Alcohol digestion. Per cent. sugar.	Water digestion. Per cent. sugar.	Difference. Per cent.
1	12.50	12.30	—0.2
2	12.65	12.59	—0.06
3	13.30	13.20	—0.1
4	11.90	11.73	—0.17
5	15.48	15.28	—0.20
6	16.00	15.79	—0.21
7	15.06	14.66	—0.4
8	11.81	11.81	0.00
9	13.23	13.44	+0.21
10	12.70	13.05	+0.35
11	13.10	13.02	—0.08
12	12.29	12.72	+0.43
13	13.54	13.24	—0.3
14	13.20	13.11	—0.09
15	11.86	12.19	+0.33
16	12.63	12.96	+0.33
17	13.88	13.64	—0.28
18	13.98	13.98	0.00
19	16.68	16.53	—0.15
Average	13.41	13.43	—0.02

[1] *Loc. cit.*, pp. 180 and 182.

The average of error between the two methods is scarcely greater in any case than would be likely to occur in ordinary duplicate analyses. Certainly the above results do not indicate that 0.2 per cent. should be deducted from all hot water digestions to give the correct data, as was maintained to the writer last winter by a German sugar chemist.

THE RICHEST PORTION OF THE BEET.

In answer to many inquiries some analyses were made tending to show what portion of the beet has the greatest sugar content. The samples were all carefully topped at the leaf line, thoroughly brushed and divided horizontally into approximately three equal portions. The samples were grated by hand, carefully mixed and analyzed by the hot water digestion method. The results are given in the following table :

No. of sample.	Upper portion of beet. Per cent. sugar.	Middle portion of beet. Per cent. sugar.	Lower portion. of beet. Per cent. sugar.
1	11.20	13.20	13.50
2	11.60	12.30	11.60
3	9.93	9.98	9.73
4	11.16	13.64	12.87
5	11.70	13.90	10.80
6	10.10	11.30	10.30
7	11.60	12.10	14.20
8	9.10	10.40	11.10
9	10.50	12.40	10.10
10	11.08	13.2	13.00
Average	10.9	12.2	11.7

Where only *portions* of beets are used to make up the sample for analysis, a full-length longitudinal section should be taken, and the same fractional portion of each beet.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

ON THIOUREAAMIDINES: A CORRECTION.

BY HENRY L. WHEELER.

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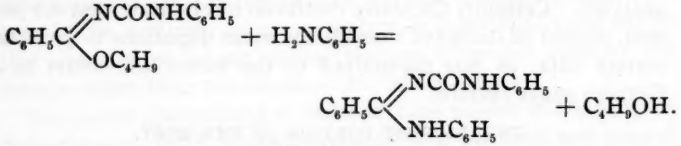
RECENTLY Wheeler and Sanders[1] published an article on ureaimido esters, thioureaimido esters, acylthioureaimido esters and ureaamidines. An examination of the behavior of the ureaimido esters towards organic bases showed that they reacted

[1] This Journal, **22**, 365.

in every case. For example, phenylureaimidoisobutyl benzoate and aniline reacted as follows :



In other words this ureaimido ester behaved in the normal manner with aniline, and an amidine was formed, as was shown by analysis. That this is correct has now been thoroughly established by the preparation of the above ureaamidine from benzenylphenylamidine[1] and phenyl isocyanate.

When the corresponding thioureaimido esters and acylthioureaimido esters were treated with aniline, β-naphthylamine, *p*-anisidine, etc., products were obtained which from analogy were assumed by the writer to be thioureaamidines, although in the five cases described the determinations of nitrogen invariably came low. It was at that time thought that these results were due to the fact that the compounds burn with great difficulty.[2]

After the above was published it was found that our analytical results agreed better with those calculated for the corresponding thiourea derivatives (column B, below) than with those of the supposed thioureaamidines (column A). The thiourea derivatives have now been prepared, and a comparison of these with our so-called thioureaamidines shows that the compounds are identical.

The following correction is therefore to be made in our work :

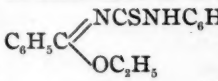
A.	B.
Benzenylphenylthiourea-*p*-anisylamidine	phenyl-*p*-anisylthiourea.
Benzenylphenylthioureaphenylamidine.....	diphenylthiourea.
Benzenylphenylthiourea-β-naphthylamidine .	phenyl-β-naphthylthiourea.
Benzenylbenzoylthioureaphenylamidine	benzoylphenylthiourea.
Benzenylbenzoylthiourea-*o*-tolylamidine.....	benzoyl-*o*-tolylthiourea.

It has also been found that the true thioureaamidines are decidedly different from our previously described products. Two examples of these have been prepared by combining benzenylphenylamidine with phenyl mustard oil and benzoylrhodanide, respectively. The action of organic bases on the thioureaimido esters,

[1] Prepared by Pechmann's method : *Ber. d. chem. Ges.*, **30**, 1782 (1897).

[2] For an example of such a case, see benzoyl-*m*-chlorphenylurea and the corresponding thiourea. Wheeler and Johnson : *Am. Chem. J.*, **24**, 220 (1900).

therefore, proceeds as follows, giving a thiourea derivative and an imido ester or its reaction products :

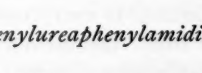


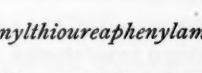
$$+ H_2NC_6H_5 =$$

$$C_6H_5NHCSNHC_6H_5 + C_6H_5C(OC_2H_5) = NH.$$

The reaction is unique inasmuch as it differs from that of both oxygen analogues and acylimido esters.[1] It may also be added that phenylthioureaimidoisobutyl benzoate gave phenylthiourea with aqueous-alcoholic ammonia ; and that benzoylthiourea was obtained from benzoylthioureaimidomethylphenyl acetate and phenylhydrazine.[2]

EXPERIMENTAL PART.

Benzenylphenylureaphenylamidine,  , was prepared by dissolving 2 grams of benzenylphenylamidine in benzene and adding the calculated quantity of phenyl isocyanate (1.2 grams), whereupon the ureaamidine separated at once. It was found to be difficultly soluble in alcohol, more readily in benzene, from which solutions it separated in the form of fine needles melting sharply from 179°–180°. It was identical in appearance and properties with the product obtained from phenylureaimidoisobutyl benzoate and aniline.

Benzenylphenylthioureaphenylamidine,  .—Two grams of benzenylphenylamidine and 1.3 grams of phenyl mustard oil were mixed, and fused on the water-bath. On warming for a few minutes, the mixture solidified. It was then crystallized from benzene, whereupon fine needles or prisms separated, melting at 138°. This material had neither the appearance nor properties of the substance previously described under this name. A nitrogen determination gave :

	Calculated for $C_{20}H_{17}N_3S$.	Found.
Nitrogen.....	12.68	12.60

Phenylthioureaimidoisobutyl Benzoate and Aniline gave a product crystallizing from alcohol in plates which melted at 151°–152°.[3]

[1] Wheeler and Walden : *Am. Chem. J.*, **20**, 568, (1898).
[2] *Loc. cit.*
[3] *Loc. cit.*

A specimen of Kahlbaum's thiocarbanilide had the same appearance and properties, and when a portion was mixed with this material the melting-point was not altered.

	Calculated for $C_6H_5C(NHC_6H_5)=NCSNHC_6H_5$. $C_{20}H_{17}N_3S$.	Calculated for $C_6H_5NHCSNHC_6H_5$. $C_{13}H_{12}N_2S$.	Found.
Nitrogen ..	12.6	12.2	12.0

This material is therefore diphenylthiourea.

Phenylthioureaimidomethyl Benzoate and Paraanisidine gave a product which, when crystallized from alcohol and amyl acetate, melted at about 180°.[1] On mixing phenyl mustard oil and *p*-anisidine, the compounds combined with evolution of heat. When the white mass, thus formed, was crystallized from amyl acetate it melted at 170°; on crystallizing then from alcohol it melted at about 180° and seemed to be identical in every respect with the compound previously obtained from the ureaimido ester and *p*-anisidine. An analysis of the substance obtained in the latter manner gave:

	Calculated for $C_6H_5C(NHC_6H_4OCH_3)=NCSNHC_6H_5$. $C_{21}H_{19}ON_3S$.	Calculated for $C_6H_5NHCSNHC_6H_4OCH_3$. $C_{14}H_{14}ON_2S$.	Found.
Nitrogen	11.6	10.8	10.1

The substance is therefore phenyl-*p*-anisylthiourea, possibly mixed with some dianisylthiourea[2] which melts at 185° and contains 9.7 per cent. of nitrogen, and which may result on repeated crystallizations of the mixed thiourea.

Phenylthioureaimidoisobutyl Benzoate and β-Naphthylamine gave a compound which, when crystallized from alcohol and amyl acetate, formed minute plates, and melted, not sharply, at 182°–183°. This compound should be phenyl-β-naphthylthiourea, which, Mainzer[3] states, melts from 155°–157°, but which melts higher on repeated crystallizations, apparently undergoing decomposition. According to Freund and Wolf[4] it melts at 165°. I have found that when phenyl mustard oil and β-naphthylamine are mixed and the product crystallized once from amyl acetate it melts at 177°–182°. On boiling this product with alcohol it melted, not sharply, from 182°–183°, and agreed in all its properties with the material obtained from the thioureaimido ester and β-naphthylamine. When the two specimens were mixed no change in melt-

[1] *Loc. cit.*

[2] Salkowski: *Ber. d. chem. Ges.*, **7**, 1012 (1874).

[3] *Ber. d. chem. Ges.*, **15**, 1417 (1882).

[4] *Ber. d. chem. Ges.*, **25**, 1468 (1892).

ing-point was observed. The result of our previous analysis follows:

	Calculated for $C_6H_5C(NHC_{10}H_7)=NCSNHC_6H_5$. $C_{24}H_{19}N_3S$.	Calculated for $C_6H_5NHCSNHC_{10}H_7$. $C_{17}H_{14}N_2S$.	Found.
Nitrogen	11.0	10.0	10.0

This material is therefore phenyl-β-naphthylthiourea.

Benzoylthioureaimidoisobutyl Benzoate and Aniline gave a product melting from 145°–146°. This is identical with benzoylphenylthiourea described by Miquel,[1] as melting at 148°–149°. Our previous analysis is appended:

	Calculated for $C_6H_5C(NHC_6H_5)=NCSNHCOC_6H_5$. $C_{21}H_{17}ON_3S$.	Calculated for $C_6H_5NHCSNHCOC_6H_5$. $C_{14}H_{12}ON_2S$.	Found.
Nitrogen	11.6	10.9	11.2

When benzenylphenylamidine was mixed, either dry or in benzene solution, with benzoylrhodanide, a small amount of well crystallized material, melting at about 162° was obtained, in addition to some varnish. As the properties of these products had nothing in common with those of the above compound, the mixture was not further examined.

Benzoylthioureaimidoisobutyl Benzoate and o-Toluidine were stated to react, giving a product melting from 116°–117°. The same product has now been prepared from benzoylrhodanide and orthotoluidine, which, as Dixon[2] states, melts at 118–119°. On mixing this with our material the melting-point was not altered. Our former analysis is annexed:

	Calculated for $C_6H_5C(NHC_6H_4CH_3)=NCSNHCOC_6H_5$. $C_{22}H_{19}ON_3S$.	Calculated for $C_6H_5CONHCSNHC_6H_4CH_3$. $C_{15}H_{14}ON_2S$.	Found.
Nitrogen	11.2	10.3	10.8

NEW HAVEN, CONNECTICUT,
February 8, 1901.

A SPECIAL CRUCIBLE FOR CARBON COMBUSTIONS.

BY PORTER W. SHIMER.

Received February 27, 1901.

IT may, perhaps, be remembered that in a former paper by the writer on "Carbon Combustions in a Platinum Crucible,"[3] the crucible was cooled externally by means of wet wick in contact with its upper part, drawing its supply of water from a circular trough kept full by the overflow from a hollow stopper.

[1] *Ann. Chem.* (Liebig), [5], **11**, 313.
[2] *J. Chem. Soc.* (London), **55**, 622.
[3] This Journal, **21**, 557, July, 1899.

By this arrangement with wet wick and water-cooled stopper, it is possible to use an ordinary platinum crucible for carbon combustions and other work in which it is necessary to heat substances to high temperatures in special atmospheres. While wet-wick is effective, it is somewhat troublesome and needs a little attention. To displace the wick and trough, I have devised a special crucible provided, in its upper part, with a platinum cooling chamber about $\frac{1}{2}$ inch wide and $\frac{1}{8}$ inch deep, having short platinum inlet and outlet tubes at opposite sides. The water, after flowing through the stopper, is conducted to the cooling chamber of the crucible by bent glass and rubber tubing, through which it flows to waste.

The rubber band, by which the crucible is tightly closed, is thus effectually cooled on its inner side by contact with the cold stopper, and on its outer side by contact with the cold top of the crucible. The lower part of the crucible may be heated to the

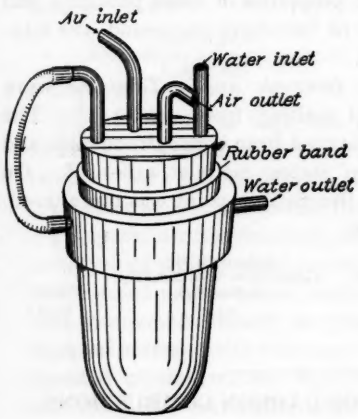


Fig 1.

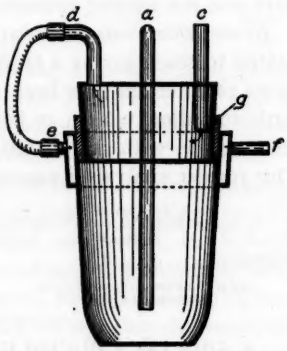


Fig 2.

full temperature of the blast-lamp without affecting the rubber in the least. In addition to the greater neatness and convenience of this form of crucible, it also has the advantage of greater stiffness by reason of the cooling chamber, and a smaller flame is needed to bring the crucible to a red heat. The flame of a good Bunsen burner gives enough heat for the combustion in air of carbon from steel. For graphite and direct combustions, of

course, a blast-lamp is necessary. Direct combustions of difficultly soluble alloys may be made very readily in this crucible by mixing the finely divided alloy with lead chromate in a small porcelain crucible and placing the latter in the platinum crucible for combustion, as practised by Mr. C. A. Buck, of the Bethlehem Steel Co.

The construction of the crucible and stopper will be readily understood by reference to Figs. 1 and 2. The air or oxygen inlet is at *a*. The cold water enters the stopper at *c*, and leaves it at *d*, from which point it is led by means of a rubber tube to *e*, where it enters the platinum chamber surrounding the top of the crucible. The water runs to waste at *f*; or, the direction of the flow of water may be reversed, the water entering at *f* and escaping at *c*. The band of pure, black rubber, such as can be had at most stationers, is shown at *g*. It is essential that these bands be of the best quality of rubber obtainable, for such a band will make an absolutely tight joint with the crucible, and one band may be used for many combustions. Before inserting the stopper into the crucible, the band should be wetted with a little water, to lessen friction and secure a tight joint.

For the determination of combined water in ores, minerals, and cements, it may be mentioned here, the circulating water must be preheated to prevent condensation of the water driven out by the ignition of the sample on the cool stopper and upper part of the crucible.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE AGRICULTURAL EXPERIMENT STATION.]

THE COMPLETE ANALYSIS OF FEEDING MATERIALS.

BY C. A. BROWNE, JR., AND C. P. BEISTLE.

Received March 5, 1901.

IN the ordinary analysis of feeding-stuffs it has been the general custom to determine only a few of the many constituents present; for the computation of rations or for the determination of feeding values an estimation of the moisture, fat, protein, ash, and fiber is all that is usually required, the percentage of undetermined matter being simply designated "nitrogen-free extract."

This method of procedure, while sufficient for many purposes, is by no means scientifically accurate, and chemists have for a

long time felt that not only should a closer study be made of the various substances, or rather groups of substances, such as ether extract, protein, and fiber, but also that more attention should be given to that large group of undetermined bodies which make up the nitrogen-free extract.

Considerable work has been accomplished along these lines during the past few years, both in this country and abroad. Good workable methods have been adopted for the determination of sugars, starch, and pentosans, and some attempts have been made towards effecting a separation of the various lignin and cellulose bodies, which make up the greater part of what is termed crude fiber. In many cases, more particularly in the analysis of grains, the percentages of the various constituents will approximate very closely 100 per cent., but in other cases, as with feeds rich in fiber, such as hay and straw or even certain cereal products, a considerable discrepancy still exists.

In the spring of 1899 a sample of distillery waste or mash was received at the Penna. Experiment Station from the Heinz Pickle Co., of Pittsburg, Pa. A portion of the sample, which was very moist and had slightly fermented, was examined for alcohol, and fixed and volatile acids; the rest of the material was dried as quickly as possible, then ground, and subjected to the customary fodder analysis with the following results:

	Per cent.
Moisture	3.83
Crude fat	10.25
Crude fiber	17.73
Ash	1.82
Protein	23.44
Total	57.07
Nitrogen-free extract	42.93

A determination of starch in the material by the diastase method gave less than 3 per cent., showing that the malting process had been quite complete. A determination of the furfural-yielding compounds or pentosans gave about 25 per cent., showing the material to be very rich in these bodies as was to be expected from the concentration which other constituents of the mash would undergo, with the elimination of the starch. There still remained, however, some 15 per cent. of material unaccounted for. This appeared to us such an unusually large

amount for a cereal product, that we were led to make a more complete study of the undetermined residuum.

In the choice of a method applicable to a case of this kind, the writers were guided, to a great extent, by a scheme of analysis devised by H. C. Sherman.[1] The scheme adopted by us in the present instance is given herewith and differs from that of Sherman in but few respects. We have divided the lignin bodies into two classes,—the lignic acids which are removable directly by NaOH, and the lignin which is removable only after chlorination. While, as Sherman says, "there may be no established chemical difference on which to rest such a distinction," we believe that there is a physiological difference, in that the lignin which is removable only after chlorination is of a more condensed variety than that removed by direct treatment with NaOH. We have also introduced the step, since an opportunity was given of studying the solvent action exercised by the alkaline solution employed in ordinary crude-fiber analysis.

SCHEME FOR THE ANALYSIS OF DISTILLERY WASTE.

(Four samples of 5 grams each were taken for analysis.)

	Per cent.	
I. Samples were dried for 8 hours at 100°C.....	Loss = Moisture,	3.83
II. Residues from I extracted with anhydrous ether 16 hours.....	Extract = Crude fat,	10.25
III. Residues from II boiled with 95 per cent. alcohol 30 minutes, cooled, made to 100 cc. with alcohol, filtered, and filtrates combined:		
	Original substance. Per cent.	
a. Extract determined in aliquot	3.62	
b. Ash " " "	0.10	
c. Protein " " "	1.20	
d. Sugars " " " (by copper reduction)....	0.00	Sugar, 0.00
Undetermined matter [*a* — (*b* + *c* + *d*)].....	2.32	
IV. Residues from III treated with water at laboratory temperature over night; made to 100 cc. with water, filtered, and filtrates combined.		

[1] This Journal, 19, 291.

e. Extract determined in aliquot	4.50	
f. Ash " " "	0.46	
g. Protein " " "	0.73	
h. Dextrin (?) " " " (by inversion and copper reduction)	2.13	Dextrin (?), 2.13
Undetermined matter [*e* — (*f* + *g* + *h*)]	1.18	
V. Residues from IV dried and weighed, then reground and the starch determined by the diastase method; residues dried and reweighed.		
i. Residue determined before diastase treatment	78.29	
j. Starch determined in extract from diastase treatment	2.66	Starch, 2.66 (?)
k. Residue determined after diastase treatment	73.87	
VI. Residues from V boiled 30 minutes with 200 cc. H_2SO_4 1.25 per cent., filtered, washed with hot H_2O and alcohol, dried, weighed, and then combined.		
l. Residues determined after H_2SO_4 treatment	45.42	
m. Protein determined in aliquot of combined residues	16.56	
n. Ash determined in aliquot of combined residues	0.95	
o. Carbohydrates in residue [*l* — (*m* + *n*)]	27.91	
VII. Aliquots from combined residues of VI boiled 30 minutes with 200 cc. NaOH 1.25 per cent., filtered, washed with hot H_2O and alcohol, dried, and weighed.		
p. Residue determined after NaOH treatment	17.94	
q. Protein determined in aliquot of residue	0.63	
r. Ash determined in aliquot of residue	0.21	
s. Carbohydrates in residue [*p* — (*q* + *r*)]	17.10	
t. Carbohydrates removed by NaOH treatment (*o* — *s*)	10.81	Lignic acids, 10.81 (?)

VIII. Residues from VII chlorinated 1 hour, then boiled 5 minutes with 2 per cent. Na_2SO_3 and 0.2 per cent. NaOH solution (method of Cross and Bevan), filtered, washed, with hot H_2O and alcohol, dried, and weighed.		
u. Residue determined after chlorination process	16.26	
v. Protein determined in aliquot of residue	0.19	
w. Ash determined in aliquot of residue.....	0.11	
x. Carbohydrates in residue $[u - (v + w)]$	15.96	
y. Carbohydrates removed by chlorination process $(s - x)$	1.14	Lignin, 1.14
z. Pentosans in residue *u* 5.62 per cent., or of original substance	0.91	
Cellulose $[u - (v + w + z)]$	15.05	Cellulose, 15.05
Pentosans determined in original substance by phloroglucin method.....		Pentosans, 24.86
Nitrogen determined in original substance 3.75 per cent., $N \times 6.25 =$ protein		Protein, 23.44
Ash determined in original substance.....		Ash, 1.84
Total.....		96.01

The sum of the various ingredients in the above table amounts to 96.01 per cent., thus leaving an undetermined residuum of about 4 per cent. It was thought at first, that the undetermined matter in the alcoholic and aqueous extracts might explain this deficiency; the sum of this undetermined matter in the above scheme, it will be seen, amounts to 3.5 per cent., and if this be estimated as resin or gum, as is sometimes done, there would remain but about 0.5 per cent. of material unaccounted for.

Before working upon this assumption, however, it was thought best to make further studies as regards the actions of the various solutions employed in the above scheme. A second series of 4 samples were carried through exactly as the first with the additional determination of the pentosans in the residues after each stage of the process. The following results were secured:

	Per cent.
I. Pentosans in original material	24.86
II. Pentosans in residue after alcohol and water treatment	22.16
III. Pentosans in residue after malt digestion	20.98
IV. Pentosans in residue after H_2SO_4 treatment	3.32
V. Pentosans in residue after NaOH treatment	0.87

It appears from the above results that several per cent. of material of a pentose nature finds its way into either the alcoholic or aqueous extracts. Such substances, owing to their marked copper-reducing power, would naturally affect the sugar or dextrin determinations. Since no copper-reducing bodies were removed by the alcohol, the inference is, that the pentoses dissolved were removed entirely by the water. The writers believe that the copper-reducing power of the aqueous extract, as shown in the scheme, was due mostly or even entirely to bodies of a pentose nature, and that a serious error may thus exist in the process usually employed for determining dextrin in feeding materials.

The undetermined matter of the alcoholic extract is no doubt made up of some unclassified constituents, such as resin, etc., and at this stage of the analysis there is probably to be found a part of the discrepancy which sometimes exists in the complete analysis of feeding materials.

Another fact in connection with the pentosan determinations is that 1.18 per cent. of pentosans disappears during the malt digestion. To test this in another way, the pentosans were determined in the extract from the malt digestion. The following results were secured:

	Per cent. of original substance.
Pentosans in extract from malt digestion	2.71
Pentosans in malt solution	1.29
Difference equals pentosans actually removed	1.42

This figure coincides very closely with the value previously given, and proves unquestionably that the malt solution does exert some solvent action upon the pentosans. In order to determine how much the removal of pentosans was due to the solvent action of water alone, a blank experiment was run, using the same amount of water as malt solution, and conducting the digestion for the same length of time; the aqueous extract was then concentrated, and a determination of pentosans made in the

usual way ; the amount thus obtained amounted to 0.85 per cent. of the original material, thus showing that a considerable amount, but not all, of the pentosans removed during the malt digestion, was due simply to the solvent action of water.

A removal of pentosans during the diastase digestion introduces somewhat of an error into the starch determination. Starch was present in the material analyzed, as was shown by the slight iodine reaction, but the percentage indicated in the scheme is undoubtedly too high. The error thus introduced into the starch determination by the solubility of pentosans, would probably never be much greater than the above case, owing to the large amount of pentosans present and the long period of digestion, which, in the present instance, was twelve hours.

From the table of pentosan determinations, it is seen that 17.66 per cent. of pentosans disappears during the treatment with sulphuric acid. The extract from this treatment was saved in order to make a comparative determination of the pentosans removed, by the copper reduction process.

The extract was diluted to 300 cc., after adding sufficient H_2SO_4 to make the total amount 2 per cent. of the solution after diluting, and the whole boiled for six hours in a 500 cc. flask connected with a condensing tube. After cooling, the solution was neutralized with dilute NaOH, using phenolphthalein, and the volume completed to 500 cc. 25 cc of this solution gave a weight of reduced copper[1] equivalent to 21.65 per cent. dextrose, which would be equivalent to 21.00[2] per cent. pentoses, or 18.48[3] per cent. pentosans.

Another point which must not be overlooked in the complete analysis of feeding materials, is the presence of furfural-yielding constituents in the material left after the chlorination process. In the scheme, the writers have estimated these bodies as pentosans, and subtracted their percentage from the percentage of fiber after chlorination, in calculating the percentage of cellulose. It may be, however, that these furfural-yielding constituents of the fiber, after chlorination, are of an oxycelluiose nature, as appears from the work of Cross and Bevan, in which case the total percentage of pentosans would need to be corrected.

[1] Allihn's method of copper reduction was followed in this and all other instances.
[2] Dextrose × 0.97. Stone : *Am. Chem. J.*, **13**, 73.
[3] Pentoses × 0.88.

In conclusion, it may be said that, while the sum of the percentages of the different constituents in many feeding stuffs does not equal exactly 100 per cent., the results are as close as could be expected with the present methods of analysis. In addition to the uncertainties of some of the analytical steps just pointed out, it should also be noted that the factors used for the calculation of protein and pentosans are more or less of an arbitrary nature, and cannot be considered absolute in the case of any particular feeding material. In view of this, and our present incomplete knowledge of many of the various proximate constituents of feeding materials, the exactness attainable in some other departments of analytical chemistry is not at present to be hoped for.

CATALYSIS IN CONCENTRATED SOLUTIONS.

By J. M. Crafts.

Received March 8, 1901.

THE study of the catalytic action of acids in very dilute solutions has led to the discovery of a number of simple relations between ionic dissociation, chemical affinity, and electrical conductivity, and the conclusion is universally accepted that the active agent is the hydrogen ion. The ratio of the velocity of the reaction to the concentration of the catalysor is nearly constant in dilute solutions of strong acids, but when ionic dissociation is diminished by increasing concentration, or in the case of weak acids by the presence of bodies which reduce the concentration of hydrogen ions, the ratio of velocity to concentration diminishes ; a small acceleration has, however, been observed when certain salts are added to the solutions of strong acids. Most of the subjects for experiments, such as the decomposition of esters, the inversion of sugar, etc., do not admit of the employment of very concentrated acid solutions, because the catalysor would then enter into the reaction, forming by-products.

It seemed interesting to study the hydrolysis of the sulphonic acids by means of chlorhydric acid and other strong acids, because here the reaction is catalytic in the sense that it is induced by the presence of a strong acid which does not enter into the final products, nor does it even form intermediate products in the same evident way as in esterification by sulphuric acid, or in the oxidation of sulphurous acid through the medium of nitrous fumes, nor does the degree of concentration of the catalysing

agent change the nature of the products, which are only sulphuric acid and hydrocarbon.

The results given below show that the rapidity of the reaction instead of being proportional to the concentration of the catalysor, rises to a thirty-fivefold greater rapidity when 38 per cent. chlorhydric acid solution is employed instead of 19 per cent., and a very remarkable result was obtained by adding to a 38 per cent. chlorhydric acid solution one-half its weight of zinc chloride, the rapidity of the reaction being then raised more than threefold.

It is thus apparent that increased concentration and other influences which must be supposed to diminish ionic dissociation, promote to a high degree the rapidity of the hydrolytic action, and this fact would point to the inference that the hydrolysis is promoted by $HCl + H_2O$, and not by the hydrogen ions, unless some other predominant and preparatory reaction can be attributed to dehydrating agents like chlorhydric acid, sulphuric acid, and zinc chloride. The study of this hypothesis has been undertaken, but seems to demand an extended series of experiments before an opinion can be formed, and it is desired to give in this preliminary notice a description of experiments which establish a sharp distinction between catalysis in dilute and concentrated solutions. It is possible that the newly observed phenomena may be quite different from catalysis and may require another name, but the old one has been made to hide so many mysteries that it will serve to cover this one also, until a new theory of the reaction can be founded upon a larger number of experiments.

I will give the results of some 150 measurements in sealed tubes chiefly at 190°, and will leave aside a larger number of experiments which were made by passing steam through sulphuric acid solutions of sulphonic acids at different temperatures.

The work will be interrupted for a few months, and it is desired to reserve the field until the projects, which will be indicated for further experiments along the same line, can be executed and the data obtained for explanation, or at least for correct formulation of this interesting reaction.

EXPERIMENTAL RESULTS.

On heating in sealed tubes at 100°, the metaxylene-sulphonic acid (1 : 3 : 4) gives an easily measurable rate of decomposition

with chlorhydric acid of concentrations varying between 43 per cent. and 13 per cent. HCl gas; and the intervals of time which it is necessary to heat in order to decompose 10 per cent. of the sulphonic acid, vary between thirty minutes and more than one hundred hours, according to the strength of the acid. Benzene and toluenesulphonic acids do not react at this temperature, paraxylenesulphonic acid acts very slowly, and the sulphonic acids of the higher homologues of benzene act too rapidly at 100°, and, moreover, these acids are only partly soluble in strong chlorhydric acid even at 100°. For these reasons the first series of determinations was made with the metaxylenesulphonic acid, $C_8H_9SO_3H + 2H_2O$. The crystals of the acid can be kept for any length of time exposed to the air with only slight hygroscopic changes of weight.

A mode of preparation, which was found much more advantageous than the passage by the barium salt, consists in using directly the solution obtained by heating, during two hours at 100°, 2 parts of common sulphuric acid and 1 part hydrocarbon. The immediate product is added cautiously, to prevent heating, to common chlorhydric acid (containing about 38 per cent. HCl) cooled to zero or below. Paratoluenesulphonic acid, the common forms of metaxylene and pseudocumene sulphonic acids, and the sulphonic acids of paraxylene and mesitylene are nearly insoluble in strong cold chlorhydric acid, and the fine crystalline precipitate can easily be washed with pure cold chlorhydric acid with little loss until entirely free from sulphuric acid. Exposure for two days on a glass plate suffices to remove all traces of chlorhydric acid, and to leave the pure sulphonic acids crystallized with their normal proportions of water of crystallization. The crystalline powder so obtained can be dissolved in water and recrystallized without change of weight. Paratoluenesulphonic acid has 1 molecule of water of crystallization; the other acids named have 2 molecules. Paratoluenesulphonic acid so prepared melts at 102°; metaxylenesulphonic acid (1 : 3 : 4) at 59.8°; paraxylenesulphonic acid melts at 86°; pseudocumenesulphonic acid (1 : 3 : 4 : 5) at 112°.

The Hydrolysis, $C_8H_{10}SO_3 + H_2O = H_2SO_4 + C_8H_{10}$.—In each experiment a weighed quantity of the sulphonic acid was sealed with a weighed quantity of chlorhydric acid, or some other substance or acid as a catalysor, in a glass tube of about 1 cm.

diameter, which had been calibrated with weighed amounts of the hydrocarbons, xylene, cumene, etc.

The determinations were made, after heating a definite period, by measuring the height of the layer of hydrocarbon set free. Certain precautions were taken relative to the solubility of the hydrocarbon in the acid solution both hot and cold, and the time required for the complete separation of the dissolved hydrocarbon on cooling. A few control determinations of the sulphuric acid set free were also made, but in this preliminary notice it is not necessary to enter into the details of these operations, because even considerable errors of measurement and impurity of the sulphonic acids would not disguise the nature of the reaction, which it is designed to show.

A well determined and constant temperature was obtained by using the ebullition of pure substances, water and benzene, under atmospheric pressure. The tubes were always heated in contact with the liquid bath, and allowance was made for the time (about three minutes) required for a thermometer enclosed in a similar tube to take the temperatures of 79° or 99°. If the test is made by plunging the glass tube, containing a thermometer and filled with liquid, in a metal tube heated by boiling water to a constant temperature but only containing air, the transfer of heat through the air layer to the glass tube is so slow that nearly an hour is required for the thermometer to reach 100°.

A. Experiments with Metaxylenesulphonic Acid qnd Chlorhydric Acid.—In the following experiments (Nos I–XIII), the temperature was 99.7°–100°. The hours from the commencement of heating and the corresponding percentages of decomposition are given. The latter was usually determined by measuring the hydrocarbon set free in a tube which had been calibrated at the same place with known weights of the same hydrocarbon. It was usually necessary to wait some hours for the complete separation of the hydrocarbon which had dissolved at a high temperature in the acid liquid, but appeared to be almost completely separated in the cold, so that the readings became constant after intervals of an hour.

I. 10 grams metaxylenesulphonic acid, $C_6H_3CH_3(1)CH_3(3)SO_3H(4) + 2H_2O$, + 75 grams chlorhydric acid (10 per cent. HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
16	0.0	136	8.7
32	2.2	156	8.7
64	4.3	172	9.4
104	5.6	212	10.0
120	6.5		

The apparent retardation of the decomposition during the first sixteen hours is probably only due to the solubility in the acid mixture of the first fraction of xylene, about 0.04 gram. If this is the case, about 1 per cent. should be added to all the measures. The decomposition with a measurable rate of speed up to about 10 per cent., and from that point a decomposition of only 0.6 per cent. in forty hours, seems to indicate the presence of an impurity, possibly $C_6H_3CH_3$ (1) SO_3H (2) CH_3 (3), which decomposes more rapidly, while the pure acid, $C_6H_3CH_3$ (1) CH_3 (3) SO_3H (4), which remains is not decomposed by 10 per cent. chlorhydric acid solution.

II. Ten grams metaxylenesulphonic acid + 75 grams chlorhydric acid (13.1 per cent. HCl). 0.43 gram xylene was added before heating in order to saturate the acid liquid, the height of the layer of xylene was noted after shaking, and was subtracted from subsequent readings.

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
16	1.9	136	10.2
32	2.4	152	12.0
48	4.2	172	13.8
64	5.4	188	15.7
88	7.9	204	17.4
104	9.0	220	18.7
120	10.2		

The series was terminated by the breaking of the tube.

III. Ten grams metaxylenesulphonic acid + 70 grams chlorhydric acid (19 per cent. HCl). No corrections were made for the solubility of xylene in the acid solution in this and in the subsequent experiments.

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	1.	144	40.5
20	6.4	160	44.6
24	9.0	176	47.8
40	14.7	192	51.1
56	20.0	208	54.8
72	21.7	224	58.1
88	25.7	240	61.0
104	30.7	256	63.8
128	36.4	272	66.3

IV. Ten grams metaxylenesulphonic acid + 30 grams chlorhydric acid (10.3 per cent. HCl) + 8.75 grams sulphuric acid.

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	1.0	96	31.8
8	2.5	112	36.2
12	4.0	133	40.8
16	7.0	155	46.3
32	12.6	175	51.9
48	17.6	191	55.4
64	23.1	231	63.9
80	27.7	279	70.4
		327	77.0

V. Ten grams metaxylenesulphonic acid + 93 grams chlorhydric acid (19 per cent. HCl) + 37.5 grams zinc chloride.

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	3.0	24	30.9
8	13.4	28	31.1
12	16.0	32	34.8
16	22.0	36	38.8
20	26.0	40	42.3

VI. Twenty grams metaxylenesulphonic acid + 90 grams chlorhydric acid (25 per cent. HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	3.6	52	55.2
8	10.0	56	58.0
12	16.0	60	60.9
16	20.3	64	64.8
20	27.1	68	67.7
24	32.0	72	69.8
28	35.6	88	77.7
32	39.2	104	84.1
36	44.9	120	86.9
40	46.3	136	90.1
44	48.1	152	91.5
48	52.0		

VII. Ten grams metaxylenesulphonic acid + 515 grams chlorhydric acid (25 per cent. HCl).

Hours.	Xylene. Per cent.
4	2
16	22
20	29

A large bulb with a narrow neck of very thick glass was used. The calibration of the somewhat conical neck was less exact, and the readings were more uncertain than in a tube.

VIII. Twenty grams metaxylenesulphonic acid + 70 grams chlorhydric acid (31.4 per cent. HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	14.2	28	83.1
8	29.7	44	92.0
12	47.6	60	96.1
16	57.9	76	95.6
20	68.3	92	95.9
24	76.9		

IX. Ten grams metaxylenesulphonic acid + 550 grams chlorhydric acid (31.4 per cent. HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
1	6.3	10	35.2
2	9.4	14	44.8
6	20.9	18	60.0

X. Twenty grams metaxylenesulphonic acid + 70 grams chlorhydric acid (38.4 per cent. HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	34.9	48	91.8
8	67.7	64	93.0
12	83.7	80	94.5
16	88.7		

XI. Ten grams metaxylenesulphonic acid + 38 grams chlorhydric acid (38.4 per cent. HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
$\frac{1}{4}$	0	$5\frac{1}{2}$	48.9
$\frac{1}{2}$	3	$6\frac{1}{2}$	56.5
$\frac{3}{4}$	5.7	$7\frac{1}{2}$	60.8
1	8.4	$8\frac{1}{2}$	66.6
$1\frac{1}{2}$	14.0	$9\frac{1}{2}$	70.6
2	18.6	$10\frac{1}{2}$	72.1
$2\frac{1}{2}$	23.5	$11\frac{1}{2}$	74.7
3	28.5	$13\frac{1}{2}$	79.7
4	37.2	$15\frac{1}{2}$	81.0
$4\frac{1}{2}$	41.0	$17\frac{1}{2}$	82.0

XII. Ten grams metaxylenesulphonic acid + 39 grams chlorhydric acid (43 per cent. HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
2	38.2	9	90.7
4	68.6	10	91.0
5	77.2	14	92.8
6	86.0	18	94.2
7	89.5	22	97.3
8	90.4	38	97.7

XIII. Ten grams metaxylenesulphonic acid + 38 grams chlorhydric acid (38.4 per cent. HCl) + 19 grams $ZnCl_2$.

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
1	28.1	6	92.2
2	55.0	10	96.4
3	75.9	14	97.5
4	86.1	18	99.8
5	90.3	34	99.4

XIV. *Temperature 80.2°.*—Ten grams metaxylenesulphonic acid + 36 grams chlorhydric acid (38.4 per cent. HCl)+ 18 grams zinc chloride.

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	6.0	20	49.6
8	15.6	24	57.5
12	27.9	28	65.3
16	38.2	32	72.2

B. Experiments with Metaxylenesulphonic Acid Heated with Sulphuric Acid at 100°.—

XV. Ten grams metaxylenesulphonic acid + 35 grams dilute sulphuric acid (25 per cent. H_2SO_4) were heated twenty hours at 100°. There was no sign of separation of xylene.

XVI. Ten grams metaxylenesulphonic acid + 112 grams dilute sulphuric acid (50 per cent. H_2SO_4).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	4.2	56	69.6
8	13.9	60	71.4
12	21.2	64	74.4
16	27.8	68	76.3
20	34.5	72	78.1
24	40.6	76	79.3
28	44.2	80	81.7
32	47.8	96	85.4
36	52.7	112	86.0
40	56.3	128	87.2
44	59.3	144	88.4
48	64.2	160	88.4
52	66.6	176	88.4

XVII. Ten grams metaxylenesulphonic acid + dilute sulphuric acid (75 per cent. H_2SO_4).

Soon after heating, the well-known phenomenon took place between the diluted sulphuric acid and the sulphonic acid: a lighter layer of a viscous liquid rose to the top, and this was

covered by a smaller layer of xylene. The viscous layer which separated contained 5.5 per cent. of dissolved xylene, and the remainder had nearly the composition $H_2SO_4 + 2H_2O$ (33 per cent.) $+ C_8H_{10}SO_3 + 2H_2O$ (67 per cent.). It is more probable, however, that most of the water should be regarded as combined with sulphuric acid, and the greater part of the metaxylenesulphonic acid must be anhydrous on account of its power of dissolving xylene. This view is confirmed by the fact that the crystalline hydrated sulphonic acid dissolves on gently warming in sulphuric acid, diluted with enough water to make 75 per cent. H_2SO_4 and then an acid separates later on heating, giving the upper viscous layer.

These experiments suggest the idea that all dehydrating agents may bring the crystalline hydrated sulphonic acids into an anhydrous state, and that the anhydrous form may exist in solution, and perhaps be more susceptible of hydrolysis than the hydrated acids. This hypothesis will be investigated.

C. Metaxylenesulphonic Acid Heated to 100° with Nitric Acid.—XVIII. Ten grams metaxylenesulphonic acid + common nitric acid, diluted with an equal weight of water, were heated three hours at 100° in a sealed tube. There was no sign of xylene, and only traces of insoluble nitro derivatives. The pressure of gas due to oxidation was not very strong.

Thus nitric acid has no action favoring hydrolysis to be compared to that of a molecular equivalent of chlorhydric or sulphuric acid.

THE RELATION BETWEEN CONCENTRATION OF THE ACID SOLUTIONS AND THE RAPIDITY OF THE HYDROLYSIS.

Curves were plotted of all these series of experiments, and the following table gives the time required in each case to decompose 5, 10, 15, etc., per cent. of the sulphonic acids.

In experiments II to XVI the first vertical column of the above table gives the percentages by weight of HCl gas in the chlorhydric acid solution; the second column gives the weights of acid solution to which in each case 10 grams of crystallized sulphonic acid were added, and the third vertical column gives for experiment IV a weight of H_2SO_4 added to the solution, while for experiments V, XIII, and XVI weights of $ZnCl_2$ were added.

The next 18 vertical columns give the hours and decimal frac-

PERCENTAGE DECOMPOSITION OF METAXYLENESULPHONIC ACID HEATED TO 100° WITH CHLORHYDRIC ACID.

	Percentage of chlorhydric acid.	Weight of liquid. Grams.	Added. Grams.	5 per cent.	10 per cent.	15 per cent.	20 per cent.	25 per cent.	30 per cent.	35 per cent.	40 per cent.	45 per cent.	50 per cent.	55 per cent.	60 per cent.	65 per cent.	70 per cent.	75 per cent.	80 per cent.	85 per cent.	90 per cent.	Velocity constant. Unit of time, 100 hours.
II.	13.0	75	.....	55.0	118.0	182.5	...	...	....	....	....	....	....	....	....	....	...	...	...	...	...	0.089
III.	19.0	70	.....	17.0	29.0	44.0	61.0	80.0	100.0	120.0	140.5	162.0	187.0	210.0	234.0	264.0	..	...	...	...	...	0.39
IV.	10.0	30	8.75 H_2SO_4	13.0	25.0	40.0	55.0	70.5	92.0	113.0	132.0	151.5	170.0	189.0	207.0	233.0	...	...	...	...	...	0.40
V.	19.0	93	37.5 $ZnCl_2$	4.5	6.5	10.0	14.0	18.5	24.0	30.0	37.5	....	....	....	....	....	...	...	...	...	...	1.43
VI.	25.0	45	.....	5.0	8.0	11.0	14.5	18.5	23.0	28.0	33.5	39.0	45.5	52.0	58.5	65.5	73.5	84.0	92.0	...	...	1.59
VIII.	31.4	35	.....	...	...	4.2	5.3	6.4	7.6	9.0	10.3	11.6	13.0	14.6	16.4	18.5	20.8	23.3	25.8	29.1	35.0	5.75
IX.	31.4	550	.....	0.8	2.2	3.6	5.0	6.6	8.3	10.0	11.9	13.9	15.4	16.8	18.0	....	...	...	...	...	...	5.10
X.	38.4	35	.....	...	...	...	...	...	...	4.0	4.5	5.0	5.5	6.1	6.8	7.5	8.5	9.5	10.8	...	...	14.1
XI.	38.4	38	.....	0.5	1.2	1.6	2.1	2.6	3.1	3.8	4.3	5.0	5.6	6.4	7.1	8.1	9.4	11.2	14.3	...	...	12.9
XII.	43.0	39	.....	...	...	...	...	...	1.8	1.95	2.1	2.3	2.6	2.8	3.2	3.7	4.0	4.7	5.2	...	...	31.0
XIII.	38.4	38	19 $ZnCl_2$	...	...	...	0.8	0.9	1.0	1.2	1.4	1.5	1.7	2.0	2.2	2.4	2 6	2 9	3.4	...	...	47.8
				When Heated to 80.1° with Chlorhydric Acid (38.4 per cent.) and 50 per cent. $ZnCl_2$.																		
XIV.	38.4	36	18 $ZnCl_2$	4.0	6.0	7.6	9.4	11.0	12.8	14.6	16.4	18.3	20 5	22.6	25.0	27.4	30.6	33.6	...	...	...	3.2
				When Heated to 100° with Sulphuric Acid (50 per cent.).																		
XVI.	50.0	35	.....	4.0	6.0	8.25	11.0	14.0	17.0	20.5	24.0	29.0	33.5	38.5	44.0	50.0	57.5	65.5	76.5	94.0	...	2.1

tions of an hour required to decompose 5, 10, 15, etc., per cent. of the sulphonic acid.

The last column gives the velocity constants calculated, not from the figures of the table, but from the means of the constants given by each experimental measure, rejecting those of less than 10 and more than 80 per cent. decomposition, because at the two extremities the results are less accurate.

A very remarkable relation appears between the velocity constants and the concentration of the chlorhydric acid which promotes the action (as a catalysor?).

For the percentages of HCl between 13 and 31 the velocity increases fourfold for each successive increment of 6 per cent. HCl. The rate appears to be less rapid for higher percentages, but the upper limit of the law may perhaps be extended by more careful measures. Unpublished experiments confirm this relation for other sulphonic acids and extend it to lower percentages of HCl.

Mathematically stated, the relation is expressed by the formula: the logarithm of the velocity constant is a linear function of the percentage concentration of chlorhydric acid.

Since the sulphonic acids have nearly as strong a chemical affinity as chlorhydric acid, it was thought that they might catalyze themselves, and the decomposition might be related to the concentration. Only two experiments have been made, but they serve to confirm this idea :

1. Five grams metaxylenesulphonic acid were dissolved in 2.5 grams of water, and were heated at 100° for forty hours. The sulphuric acid set free was 1.9 per cent. of the amount corresponding to complete decomposition. No xylene was visible in the tube, but it separated out on diluting with water.

2. Five grams of metaxylenesulphonic acid were dissolved in 100 grams water and heated to 100° for forty hours. The sulphuric acid set free was only 0.1 per cent. Thus concentration in these experiments gives rise to a rapidly increasing rate of decomposition.

With metaxylenesulphonic acid a change of position of the SO_3H group, if such change can be brought about catalytically, would complicate the reaction, since the susceptibility to decomposition is greatly increased, when the SO_3H group is placed between the two side-chains.

The series of experiments will be extended to other tempera-

tures and the more tedious, but likewise more accurate, method of weighing the sulphuric acid set free instead of measuring the amount of hydrocarbon will be used.

If we attempt to estimate the differences and the similarities in the modes of catalytic action of strong acids in concentrated or in weak solutions, it will be convenient to do so under the headings of Ostwald's definition of catalysis.

1. *Reactions Which Are Accelerated or Retarded by Catalysis Take Place Also without a Catalysor.*—Experiments are evidently impossible with substances which take years for the transformation of 1 per cent., and conclusions can usually only be drawn from the form of reaction curves of measurable velocities, but it appears probable that the regularity of the decomposition of sulphonic acids without by-products will make it possible to obtain useful observations near the border line, where the action is almost imperceptible.

2. *Reactions in Opposite Directions Leading to an Equilibrium Must Be Equally Influenced by Catalysis.*—The hydrolysis of sulphonic acids in presence of sulphuric acid and water would belong under this rule if the reaction were reversible, but this is probably not the case since the synthesis is direct, while the decomposition is indirect by influence of H_2SO_4 (catalysis?). The data for 50 per cent. sulphuric acid given in the preceding table show that the limit of the action is very near complete decomposition, 88 per cent., while experiments made by heating xylene with sulphuric acid of 50 per cent. concentration to 100° proved that the reverse action does not take place perceptibly.

Even the action of a 75 per cent. sulphuric acid solution on xylene is an exceedingly slow one and stops when only a few per cent. of the xylene are transformed into the sulphonic acid. The hydrolysis of sulphonic acids by means of chlorhydric acid tends to complete decomposition, nor can any evidence be obtained of an inverse reaction.

3. *The Catalytic Influence is Nearly Proportional to the Concentration of the Catalysor.*—The chief object of this paper is to show that this rule does not apply to the case of concentrated acids, and that here the facts are directly opposed to the assumption that hydrolysis is caused by hydrogen ions. In the experiments cited the relation between concentration of acid and effect rises like the tension of a gas partially combined with water and the

effect of high concentration in aqueous solution of chlorhydric acid alone, and especially with addition of zinc chloride, recalls the activity imparted to gases condensed on platinum or palladium. Ostwald discusses the action of these metals under the same heading as catalysis attributed to the ions of hydrogen, iron, manganese, etc., and OH ions, and also places ferments and enzymes beside them, saying there is no great doubt that the laws governing the action of these bodies are not essentially different from those of inorganic catalysors.

Taking these definitions together, they apply in very few points to the case of hydrolysis by concentrated acids.

The question of ionic dissociation presents new aspects in this case. Usually the compounds subjected to catalysis have been like sugar and esters, incapable of any marked degree of dissociation in aqueous solution. The sulphonic acids, on the contrary, are dissociated to nearly the same degree as the strongest acids, when in dilute solution, and although very little is known of the dissociation of strong acids in concentrated solution, it well may be considerable. If hydrolysis only takes place upon undissociated molecules, then the increased rapidity due to high concentration of the acid solution and to addition of zinc chloride may be ascribed to the prevention of the dissociation of the catalyzed body, while that of the catalysor subsists to a certain degree.

Experiments at different temperatures and with more sensitive bodies like mesitylenesulphonic acid which acts at low temperatures and with weaker acids, may throw some light upon this subject.

The usefulness is evident of a minute study of the difference of behavior of the sulphonic acids, for it may obviously lead to methods of separation of the hydrocarbons and the acids. Several authors have described such methods for the separation of meta- and paraxylene, and I have found during this series of experiments that mesitylenesulphonic acid, when heated to 80° for fifteen minutes with 38 per cent. chlorhydric acid, is almost wholly decomposed, while pseudocumenesulphonic acid, heated under the same circumstances, gives no sign of the separation of pseudocumene after five hours. Armstrong has used this difference of action to separate the two hydrocarbons by heating their sulphonic acids with chlorhydric acid at 100°, but the statement attributed to him in Beilstein II, 29, is incorrect; namely, that

pseudocumenesulphonic acid is not decomposed by heating for one hour with strong chlorhydric acid at 100°. There is difficulty in getting the rate for the first hour, because the pseudocumenesulphonic acid does not dissolve rapidly in strong chlorhydric acid at 100°, but the following determinations show the rate for subsequent hours:

Ten grams pseudocumenesulphonic acid, heated to 100°, with 35 grams chlorhydric acid (38.4 per cent. HCl), gave the following results:

Hours.	Pseudocumene. Per cent.	Hours.	Pseudocumene. Per cent.
1½	24.7	6½	95.9
2½	42.3	7½	101.6
3½	61.8	8½	103.8
4½	76.6	9½	100.3
5½	90.5	10½	100.3

The impossible results, 103.8 per cent., etc., may be due to the fact that a small amount of anhydrous sulphonic acid separates out and dissolves in the layer of hydrocarbon and is only slowly decomposed. All the results are too high for the same reason and a similar error, but a very small one, attaches to the preceding experiments with xylene. The fact that pseudocumenesulphonic acid loses a little water on long standing may also account for the above result.

Armstrong's observations were undoubtedly exact, but he is misquoted by Beilstein. He really states[1] that an oily layer is formed by adding water to the immediate product of the action of sulphuric acid upon pseudocumene and this oil, added to an equal volume of common chlorhydric acid, is not decomposed by heating one hour to 100°. No strength of acid is given, but the oily layer so described contains anhydrous pseudocumenesulphonic acid in solution in aqueous sulphuric acid, and the water present probably suffices to dilute the acids to the point where no perceptible decomposition takes place during one hour at 100°.

The name catalysis has been used after much hesitation, and it is only meant to imply that the rapidity of the action does not seem to be determined by the ordinary chemical forces of the bodies undergoing change, but rather that these forces are set in action in a peculiar way by an outside agent.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY, BOSTON,
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[1] *Ber. d. chem. Ges.*, **11**, 1697.

COMPOUNDS OF METHYL SULPHIDE WITH HALIDES OF METALS.

By Francis C. Phillips.

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WHEN methyl sulphide is added to a solution of palladium dichloride a voluminous yellow precipitate is produced, which is apparently flocculent, but upon microscopic examination is seen to consist of very fine indistinct crystals.

If the liquid containing the precipitate is heated, the precipitate redissolves, giving a liquid of a bright orange color. On cooling, this solution deposits orange-colored needle-shaped crystals which may be washed and dried, apparently without change, and are stable in air and unaffected by light. The crystals are quite soluble in boiling water, but very slightly soluble in the cold.

An analysis of the crystals was made in the following manner:

A portion of the substance was dissolved in water and a current of carbon monoxide passed through the solution, which was kept upon a water-bath. Metallic palladium was precipitated. This was filtered through an asbestos filter, previously weighed. After drying, the metal was heated in a stream of hydrogen, and then, without admitting air, dry nitrogen was passed through the tube, and the metal finally allowed to cool in the stream of nitrogen. Experiments demonstrated that the finely divided palladium could be thus easily brought to constant weight. The nitrogen used was prepared from air by the use of alkaline pyrogallate to remove oxygen, and subsequent passage over a heated mixture of copper and copper oxide. The hydrogen chloride in the filtrate from the palladium was neutralized by zinc and the chlorine then determined volumetrically by silver nitrate solution.

The determination of sulphur presented difficulties. Many experiments were made in attempts to oxidize the sulphur of the compound to sulphuric acid by fusion with various mixtures of alkaline carbonate with nitrate and chlorate, and with sodium peroxide. All these experiments proved fruitless, as in every case a portion of the sulphur was lost by volatilization. Heating with nitric acid in a sealed tube, failed to yield complete oxidation, even at temperatures which involved danger to the tube. The ordinary reagents which might be looked to for the

conversion of sulphur into sulphuric acid, are of little use in the case of alkyl sulphides and their compounds. The most feasible method seemed to be by direct combustion in oxygen, and this was attempted in the following manner: The substance contained in a porcelain boat was placed in a porcelain combustion tube which was heated to a high temperature in a furnace. The front end of this tube passed through a cork in the neck of a nitrogen flask, containing a solution of sodium hypobromite. To permit of this mode of connection, it was necessary to place the furnace in a strongly inclined position. The products of the combustion passed through a roll of platinum gauze, 10 cm. long, rolled tightly, and completely filling the cross-section of the combustion tube. After passing the sodium hypobromite solution in the nitrogen flask, the products were led into a bottle of 7 liters' capacity containing a little bromine water. A soft cork, soaked in melted spermaceti, served to connect the side tube of the nitrogen flask with that leading into the large bottle. Thus rubber tube connections were wholly avoided. The sodium hypobromite solution together with the washings of the large bottle and combustion tube were acidulated, evaporated, and the sulphur determined by weighing as barium sulphate.

Experiments were tried also in heating the methyl sulphide compound in carefully purified hydrogen. The same apparatus and reagents were used as in case of the employment of oxygen, the hydrogen sulphide produced being then oxidized by the sodium hypobromite to sulphuric acid. There seems, however, to be some danger of dissociation of the hydrogen sulphide and possible deposition of sulphur in the colder parts of the combustion tube. Determinations by the methods described yielded the following results:

	Per cent.
Palladium	35.09
	35.19
Chlorine	23.75
	23.57
	23.65
Sulphur	21.57
	21.40
	21.41

The analytical results indicate for the compound the composition $PdCl_2{}_2(CH_3)_2S$, the calculated percentages in the case of such a compound being:

	Per cent.
Palladium	35.41
Chlorine	23.46
Sulphur	21.22

The above formula is similar to that given by Enebuske[1] to the compound of methyl sulphide with platinous chloride, $PtCl_2(CH_3)_2S$. The palladium chloride methyl sulphide is quite stable in solid form. In solution it is susceptible to the same changes as those undergone by palladium dichloride. In solution it is reduced by carbon monoxide and more slowly also by hydrogen. In the solid state it is reduced by hydrogen in the cold, with setting free of methyl sulphide and hydrogen chloride.

One hundred grams of water dissolved at 26.1° C., 0.15 gram of the compound. The solution in water and also the dry substance possess a slight odor of methyl sulphide. It is soluble in a great number of organic liquids, including benzene, ether, alcohol, chloroform, acetone, ethylene dibromide, carbon disulphide, methyl iodide, commercial amylene, and gasoline. It fuses at 124° C., solidifying again on cooling to a red crystalline mass. It seemed to be of interest to learn something of the products of its decomposition by heat. For this purpose, it was heated in nitrogen. At 250° an evolution of methyl sulphide began, and continued until the temperature rose to 260°, when a black residue was left, which proved on analysis to consist of nearly pure palladious sulphide. The gas escaping at the higher temperature, after being passed through water to remove any hydrogen chloride which might be present, was led through a glass tube containing sodium carbonate heated to redness. The sodium carbonate was afterwards tested and found to have absorbed chlorine. When the escaping gas was led through a solution of potassium hydrosulphide, methyl hydrosulphide was easily detected by its reactions toward ammoniacal solutions of silver nitrate and of copper sulphate. It was found that hydrogen chloride is not evolved on heating the compound. Hence, as chlorine had been found, and also the radical methyl, the compound methyl chloride was indicated. Moderately heated, therefore, the compound yields up a portion of its methyl sulphide. At a more intense heat it yields methyl chloride, palladium sulphide remaining as a residue.

As regards the constitution of the compound, it would seem

[1] *J. prakt. Chem.*, [2], **38**, 358 (1888).

that the sulphur of the methyl sulphide might be tetravalent. The formula might possibly be written:

$$(CH_3)_2{=}S(Cl){-}Pd{-}S(Cl){=}(CH_3)_2.$$

This is improbable, however, because the compound seems to contain chlorine linked with palladium, since hydrogen reduces the dry compound in the cold, just as it reduces dry palladium chloride, yielding hydrogen chloride in both cases.

It seemed to be of interest to study other compounds of methyl sulphide with halides of metals. The literature of the subject is scanty, little attention having been given to compounds of this class, since Loir[1] in 1853 described the compounds of methyl sulphide with mercuric chloride and iodide, and with platinic chloride.

For the preparation of the compounds described in this paper, it was necessary to obtain pure methyl sulphide. This was made by the method of Klason,[2] by distilling a mixture of sodium methyl sulphate with sodium sulphide.

COMPOUND OF METHYL SULPHIDE WITH MERCURIC CHLORIDE.

On adding methyl sulphide to a solution of mercuric chloride, a bulky precipitate of a white color is produced, which is seen under the microscope to be made up of indistinct crystalline needles. Exposed in a dry state to sunlight, the substance becomes somewhat darker in color. If preserved for some time in the solution in which it has been formed, it assumes a much more decidedly crystalline character. It is slightly soluble in water and more soluble in alcohol. The solution has a slight odor of methyl sulphide. It is slightly soluble in chloroform, carbon disulphide, ethylene dibromide, commercial amylene, benzene, acetone, and in petroleum gasoline. The solution in water yields a heavy yellow precipitate with caustic alkalies, and in other respects, the reactions in solution are similar to those of mercuric chloride.

Its melting-point varies with the rate of heating, as it undergoes partial decomposition, losing some of its methyl sulphide. When heated rather rapidly the lowest melting-point observed was 150°–151°, but if the heat is applied more slowly, its color

[1] *Ann. Chem. u. Pharm.*, **87**, 369 (1853); *Compt. rend.*, **34**, 1095.

[2] *Ber. d. chem. Ges.*, (1887), 3406.

grows darker, and as the result of a partial decomposition it melts at a varying and much higher temperature.

Heated in purified nitrogen it gives off methyl sulphide at about 150°, and at 170° white needle-shaped crystals form as a sublimate. No sulphide of mercury is formed as a result of heating. In the analysis of the compound the sulphur was determined by combustion in oxygen, as described in case of the palladium compound. Mercury was determined by precipitation of the aqueous solution by hydrogen sulphide and weighing as mercuric sulphide. Chlorine was determined by decomposition of the compound by zinc in presence of water and titration by silver nitrate solution. The results of the analysis are as follows:

	Per cent.
Mercury	64.27
	64.07
	64.19
Chlorine	22.26
	22.68
	22.66
Sulphur	6.63
	6.84
	6.76
	6.73

Other determinations were made in the case of the same compound after crystallizing from alcohol. The results were:

	Per cent.
Mercury	64.41
	64.31
Chlorine	22.60
	22.53

The calculated percentages in the case of a compound having the formula $3HgCl_2, 2(CH_3)_2S$ are as follows:

Mercury	64.63
Chlorine	22.70
Sulphur	6.42

Loir[1] assigns to the compound, obtained on adding methyl sulphide to mercuric chloride, the formula $HgCl_2(CH_3)_2S$. Analyses have been made of many preparations of the mercuric chloride methyl sulphide compound, but in no case has a product been obtained having the composition stated by Loir.

[1] *Loc. cit.*

COMPOUND OF METHYL SULPHIDE WITH CUPROUS CHLORIDE.

When methyl sulphide is added to a concentrated solution of cupric chloride, the color of the liquid changes from green to dark brown, and heat is evolved. After standing for a few hours, a mass of white crystalline scales forms at the bottom. The compound, if rapidly washed and dried, is white, but it is liable to turn to a yellowish green during drying. Exclusion of air does not serve completely to prevent this change of color. The crystals are almost insoluble in water, and are very slightly soluble in the various organic liquids mentioned in connection with the mercury compound. Boiling with water seems to expel part of the methyl sulphide. The substance dissolves in ammonia and in nitric acid.

Caustic alkalies decompose it, yielding an insoluble brownish red powder. Digestion of the substance with hydrogen sulphide, gradually changes it to copper sulphide. This reaction was made use of for a determination of the copper, the sulphide being ignited, redissolved, precipitated by sodium hydroxide, and weighed as cupric oxide. Chlorine was determined in the filtrate from the copper sulphide by the method already mentioned. As there seemed to be a possibility that the chlorine might be linked to carbon rather than to copper, and that consequently it might not be fully set free as hydrochloric acid in decomposing the compound by hydrogen sulphide, determinations were also made by heating the substance in a combustion tube traversed by a stream of hydrogen, absorption of the hydrogen chloride produced in water, neutralization by zinc and titration by silver nitrate solution. Determinations were also made by decomposition of the copper chloride compound by magnesium powder and titration of the chlorine as magnesium chloride. Sulphur was determined by the method of combustion in oxygen already described. The results of analysis were as follows:

	Per cent.	
Copper	39.12	
	39.13	
Chlorine	21.85	Decomposition of the compound by hydrogen sulphide.
	21.80	
	21.76	Decomposition by magnesium.
	21.77	
	21.76	Decomposition by heating in hydrogen.
	21.60	
Sulphur	19.62	
	19.70	

The calculated percentages of the constituents named in the case of a compound having the composition $CuCl(CH_3)_2S$ are :

	Per cent.
Copper	39.46
Chlorine	22.00
Sulphur	19.90

Cuprous chloride methyl sulphide heated in nitrogen gives off methyl sulphide at about 100° C., and continues to lose methyl sulphide until the temperature reaches about 200° C. After heating to a somewhat higher temperature the chlorine present in the residue in one experiment was found to amount to 21.53 per cent. of the original weight of the portion of the compound employed.

At a temperature above 400° the compound yields a mixture of copper sulphide and copper in wire form. The reaction occurring between methyl sulphide and the solution of cupric chloride which leads to the formation of the compound $CuCl(CH_3)_2S$, is characterized by great intensity as evidenced by the heat evolved and by the promptness of the change. One-half of the chlorine in the cupric chloride is eliminated and in its stead methyl sulphide becomes linked to the copper. Apparently, therefore, the substance resulting should be a cupric compound. Judged by its white color and its chemical properties it is, apparently, to be classed as a cuprous and not as a cupric compound. Yet it does not seem probable that the copper atoms can be in this case linked as is supposed to be the case in cuprous chloride, $\begin{matrix} Cu—Cl \\ | \\ Cu—Cl \end{matrix}$. The constitution of the compound might perhaps be expressed by the formula

$$\begin{matrix} Cu—Cl \\ | \\ S=(CH_3)_2 \\ | \\ S=(CH_3)_2 \\ | \\ Cu—Cl \end{matrix},$$

in which the sulphur appears to be tetravalent. The copper atom is no doubt linked more firmly to the chlorine than to the sulphur of the methyl sulphide. The question as to the classification of the compound as cuprous or cupric, seems to depend merely on whether there are one or two carbon atoms linked to

the copper atom. The linking of a chlorine atom, together with the sulphur atom of a methyl sulphide group to a copper atom, seems to impart to the compound a cuprous character as if the chlorine atom alone were present.

COMPOUND OF METHYL SULPHIDE WITH GOLD CHLORIDE.

When methyl sulphide is added to a solution of auric chloride, much heat is evolved, and an escape of hydrogen chloride occurs while an apparently flocculent white precipitate is produced. This precipitate is insoluble in water, but slightly soluble in alcohol. It may be washed and dried at room temperature by gas light. It is rapidly decomposed by sunlight, yielding metallic gold, methyl sulphide, and hydrogen chloride. If preserved in a dark place for a few weeks in the solution in which it was formed, and in presence of a slight excess of methyl sulphide, it assumes the shape of colorless crystalline needles.

It dissolves in various organic liquids, but the solutions soon deposit metallic gold. A determination of gold was made by exposing the substance under water to direct sunlight. The gold was rapidly reduced and was filtered out, burnt, and weighed in the metallic state. The chlorine was determined volumetrically in the filtrate from the gold. The sulphur was determined by combustion in oxygen, and weighing as barium sulphate.

The following analytical results were obtained :

	Per cent.
Gold	67.16
	66.98
	66.77
	67.42
Chlorine	12.32
	12.35
	11.97
	11.74
Sulphur	10.99
	10.88

These results suggest the composition $Au\begin{matrix}Cl\\ \diagdown\!\!\diagup\\ S(CH_3)_2\end{matrix}$, since calculation shows that such a compound would contain :

	Per cent.
Gold	66.90
Chlorine	12.02
Sulphur	10.87

The gold compound was heated in nitrogen, when it was found that an evolution of methyl sulphide begins at about 100° and continues until the temperature approaches 200°. At higher temperature, pure gold is left as a residue.

The reaction leading to the formation of the gold compound resembles that by which the copper compound is produced, in that the auric chloride undergoes reduction, and the aurous chloride then unites with methyl sulphide. A trivalent gold atom appears to have its affinities satisfied partly by a chlorine atom, and partly by the sulphur atom of a methyl sulphide group.

It seems that in the compounds which have been here mentioned the metal is more firmly linked to the halogen than to the sulphur of the methyl sulphide, and that the part played by the methyl sulphide is somewhat like that of water in various hydrated salts. Ferrous chloride remains a ferrous compound no matter what may be the number of water molecules with which it combines.

Hydrated magnesium chloride is well known to lose hydrochloric acid on strong heating and in a somewhat analogous fashion some of the compounds of metallic halides with methyl sulphide decompose on heating into metallic sulphide and methyl chloride.

A further study of compounds of alkyl sulphide with other metallic halides is in hand.

My acknowledgments are due to Mr. J. C. Fetterman, assistant in this laboratory, for his skill and careful attention to details in conducting many difficult and somewhat tedious analyses in connection with this work.

A NEW METHOD FOR THE ESTIMATION OF SOLUBLE NITROCELLULOSE IN GUNCOTTON AND SMOKELESS POWDER.

By K. B. QUINAN.

Received February 28, 1901.

A SHORT review of the methods now in use for the estimation of soluble nitrocellulose in guncotton and smokeless powder may be of interest to those who are not familiar with the subject under consideration. For this reason a brief description will be given here of the two methods most generally in use; namely, the (so-called) aliquot method, and the residual method which is

at present in use by the United States government as the official method.

The first-named method is essentially as follows: A weighed portion, about 1 gram, of the dried and finely divided sample of guncotton, or colloided powder is placed in a vessel of suitable shape, provided with a tight glass stopper, and is treated therein with 250 cc. of a mixture of ether-alcohol 2 : 1 by volume. The contents of the vessel are thoroughly agitated by shaking until all the soluble nitrocellulose is in solution. An aliquot portion of this solution is now taken and placed in a small tared Erlenmeyer flask, of about 100 cc. capacity, and is evaporated to dryness therein at a temperature of 65.5° C., the final drying being made at 100° C. The Erlenmeyer flask is now cooled and weighed and the percentage of soluble nitrocellulose calculated from the weight of the colloid so obtained.

Although this method, as used in this laboratory, gives very accurate results, the opportunities for errors are many and various, and it requires much care to avoid them.

The second method, referred to as the residual method, gives very unsatisfactory results. It is essentially as follows (taken verbatim from the United States government syllabus): "About 1.5 grams of the finely divided, dry sample are treated in a covered beaker or other suitable vessel, with 250 cc. of a mixture of 1 volume absolute alcohol, C. P., and2 volumes of strongest ether, C. P., with frequent stirring, for not less than two hours. (Four hours are frequently necessary for complete solution.) The vessel is kept covered to prevent loss by evaporation. The residue is allowed to settle and the supernatant liquid decanted through an asbestos filter, made from well purified asbestos fiber. The filter is placed in the neck of a flask or otherwise protected to avoid loss of solvent by evaporation during filtration.

"The residue in the flask is then treated with a further quantity of 200 cc. of ether-alcohol mixture, and again thoroughly stirred until extraction is complete; and the whole mass is then settled. The clear liquid may be decanted, and the remainder filtered through the asbestos fiber and well washed by successive portions of ether-alcohol. The filter is then partially dried at 40° C., and the drying completed by exposure to a temperature of 100° C. for two hours. The loss (minus any volatile matter, if present) represents soluble nitrocellulose."

The main difficulty encountered in the operation of this method is the filtration of the thick colloid formed by the guncotton and ether-alcohol. It is practically impossible to effect the passage of the thick colloid through an asbestos filter without the aid of great pressure, and a large expenditure of valuable time, for the filtration is extremely slow even under the most favorable conditions. Another strong objection to the method lies in the fact that it usually requires four or five days for the completion of an analysis by this method, which renders it practically valueless for manufacturers.

The above outlined syllabi are merely intended to convey a general idea of the methods in use, and to show in a general way the objections to each method. It was to overcome these objectionable features in the methods above described that the following method was devised by the writer, which may be termed the "centrifugal method."

As far as the author is aware, the theory of centrifugal sedimentation has never as yet been applied to this particular subject. The application of this theory to the analysis of smokeless powder is as follows:

APPARATUS.

The apparatus consists of a centrifugal machine, essentially as

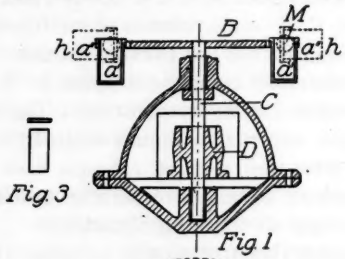


Fig. 3

Fig. 1

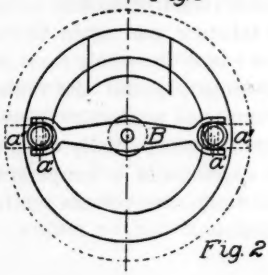


Fig. 2

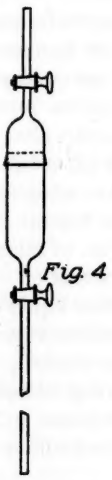


Fig. 4

per attached sketch. The vertical driving shaft (C) carries at its upper extremity a horizontal arm (B), at its lower extremity the driving pulley (D). To each end of the horizontal arm (B) are attached adjustable cups ($a'a'$) arranged on side pivots, so that they may assume a horizontal position when in motion.

	Length.	Diam.	Width.	Depth.	Thick.	Material.
Driving shaft (C)	$16\frac{3}{8}''$	$1\frac{1}{4}''$	.....	.....	..	Machine steel
Horizontal arm (B)	$17''$	.....	max $3\frac{1}{4}''$ / min $1\frac{1}{4}''$	.....	$\frac{1}{2}''$	Forged steel
Pulley (D)	..	$4\frac{1}{4}''$	$5''$	.....	..	Cast iron
Fixed cups ($a'a'$)	..	inside–$2''$	.....	inside–$4''$	..	Steel
Bearing (M)	..	$\frac{1}{2}''$	$\frac{1}{2}''$	.....	..	Steel

Revolutions per minute of arm (B)	2000
Total centrifugal force at (h)	450 lb. (about)
Power required	$\frac{1}{2}$ H. P. (about)
Cost of construction	$110.00 (approx.)

	Diam. Int.	Depth. Int.	Thickness of walls.		Weight.
Aluminum cups, Fig. 3.	$1.9''$	$4\frac{1}{8}''$	$\frac{3}{100}''$	Plane bottom	$1\frac{1}{2}$ oz. max.

	Length over all.	Length of bulb.	Diameter of bulb.	Length between cocks.	Material.
Vacuum pipette, Fig. 4.	$25\frac{1}{2}''$	$6\frac{3}{4}''$	$1\frac{3}{4}''$	$10''$	Glass

OPERATION.

About 1 gram of the finely divided (dry) sample of guncotton or smokeless powder, which is to be analyzed, is weighed on a watch-glass and is transferred to the aluminum vessel (Fig. 3) which has previously been thoroughly cleansed and dried. (Or the sample may be weighed into the aluminum vessel direct, if so desired.) To this is added 50 cc. of alcohol and the sample is thoroughly stirred to bring it into suspension. 100 cc. of ether are now added to the mixture in the cup, and the whole is then stirred for several minutes.[1] After removing the stirring rod, the aluminum vessel containing the solution is placed in one of the cups ($a'a'$) of the centrifugal machine (Fig. 1) and is covered by a loosely fitting aluminum cap. In the other cup of the centrifugal machine is placed a second aluminum vessel, containing a second sample which has been treated in the above described manner. (In this way two determinations may be carried on at the same time.) The centrifugal machine is now started gradually and allowed to remain running at top speed for ten to twelve minutes. This has been found to be a sufficient length of time for the complete sedimentation of all in-

[1] See last paragraph as to solvents.

soluble matter in the solution. The machine is now stopped gradually, and the aluminum vessels are removed from the cups (*a'a'*) and placed in a convenient position before the operator. All insoluble matter will now be found in the bottom of the aluminum vessels, and the perfectly clear supernatant liquid may be drawn off to within a quarter of an inch of the bottom of the aluminum vessels. This is done by means of the vacuum pipette shown in Fig. 4. The air in the bulb of this pipette is exhausted by means of an air-pump before use. The advantage gained by using the vacuum pipette is very easily seen, for when the lower end of the pipette is submerged in the clear liquid in the aluminum vessel and the lower stop-cock is opened, the clear solution from the vessel at once rises in the tube and passes into the bulb of the pipette. By lowering the pipette from time to time, nearly all the supernatant liquid may be drawn up into the bulb without disturbing the precipitate in the bottom of the vessel. If, however, the precipitate is disturbed it will at once be noticed as it rises in the tube clouding the clear liquid. If this should take place, the lower valve is immediately closed, thus preventing the access of the insoluble matter to the clear liquid in the bulb. The upper valve is now opened, thus releasing the tension in the bulb, so that when the lower valve is cautiously opened and a few drops of the liquid are allowed to run out of the tube and into the aluminum vessel, they carry with them all suspended matter which may have been drawn into the tube. In this way all opportunity for loss of insoluble matter is avoided. There now remains in the aluminum vessels about 10 or 15 cc. of colloid solution and a film of insoluble matter on the bottom of the vessels. Stir this insoluble matter up from the bottom of the vessel with a glass stirring rod, wash the rod thoroughly by means of a wash-bottle filled with pure ether-alcohol, and at the same time rinse down the sides of the aluminum vessels with the ether-alcohol from the wash-bottle. Now add about 50 to 75 cc. of fresh ether-alcohol to the mixture in the vessels, stir it up, place in the centrifugal, and again proceed in the manner already described. This operation should be repeated several times until all traces of soluble matter have been removed. Seven or eight washings usually suffice to remove entirely all soluble matter. Samples containing a high percentage of insoluble matter may require twelve or more washings to complete extraction.

After the extraction has been completed the insoluble matter is transferred to a weighed Gooch crucible provided with the usual asbestos pad, is dried therein at 100° C., and weighed. If preferred, the insoluble matter may be dried and weighed directly in the aluminum vessel in which the extraction was performed. The only objection to drying and weighing directly in the aluminum vessel is that this vessel cannot be ignited.

The whole time required for an analysis by this method, exclusive of the time required for drying, is from one to two hours. The average time which has been found necessary to complete an analysis is about one and one-quarter hours, for it will readily be seen that in each successive extraction, the viscosity of the solution decreases, and consequently the sedimentation is much more rapid toward the end of the analysis than it was in the beginning. For instance, the first solution obtained is a thick colloid and requires about ten or twelve minutes in the centrifugal for sedimentation, but with the second solution, about eight minutes in the machine will suffice.

This method is equally applicable to the estimation of acetone-soluble nitrocellulose, the operation being the same as in the case of the ether-alcohol extraction already described.

The results obtained by this method have been highly satisfactory both for accuracy and rapidity.

The following analyses were made on a sample of nitrocellulose containing a known amount of insoluble matter:

No. of analysis.	Insoluble matter found. Per cent.	Insoluble matter required. Per cent.
2664	0.54	0.69
2665	0.50	(Determined by aliquot method.)
2666	0.59	
2667	0.53	

These results may be improved upon by further experience with the method.

In laboratories where power is not available, the form of the centrifugal machine herein described may be modified, and provided with gear so as to admit of its being run by hand. The use of power is, of course, preferable. This syllabus is based upon the results obtained with a machine of the dimensions herein described.

In order to make the laboratory analysis analogous to the process of manufacture, the solvents used should be of the same

strength as those ordinarily used in manufacture. Care must be taken, however, that the solvents are free from all matter not volatile at 100° C.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF APPLIED SCIENCE, NO. 39.]

COMPOSITION OF TEXAS PETROLEUM.

BY CHARLES F. MABERY.

Received February 9, 1901.

INDICATIONS of the presence of petroleum in Texas in several sections have been observed during the last thirty years, and many attempts have been made to obtain oil in sufficient quantities for the preparation of commercial products. But it is only within the last six years that oil has been found in sufficient amounts to encourage further development. The principal yield has been in the counties of Navarro, Bexar, Nacagdoches, and Hardin, and the chief supply has come from the Corsicana field in Navarro County. In the early development of the Corsicana field a specimen of the oil was briefly examined by Thiele,[1] who gave its specific gravity as 0.8296, and the proportions in temperatures Fahrenheit in which it distilled. The resemblance of this oil to Pennsylvania and to Ohio petroleum alluded to by the author seems to be scarcely supported by the meager examination.

Corsicana oil was later examined by Richardson,[2] who obtained percentages of carbon and hydrogen in the distillate 100°–150° at 25 mm., corresponding to the series C_nH_{2n}.

Another important section of the Texas oil field has recently been developed in Jefferson County, and it has suddenly become famous by the discovery of a large pool, under high pressure, that has furnished the phenomenal supply in the Lucas well. The surface indications in this section, in the vicinity of Sabine Pass, were such that this pool narrowly escaped previous discovery by other prospectors. Oil has been obtained in smaller amounts for some time in this county, and the composition of one specimen was ascertained by Mabery and Buck.[3] This oil was found to consist mainly of the series of hydrocarbons represented by the general symbols C_nH_{2n-2} and C_nH_{2n-4}. It was an extremely heavy petroleum, specific gravity 0.9500. Scarcely any distilled below

[1] *Am. Chem. J.*, **22**, 489.
[2] *J. Soc. Chem. Ind.*, February, 1900.
[3] This Journal, **22**, 553.

250° atmospheric pressure. Having obtained a quantity of oil from the Lucas well before it was capped, I was interested to ascertain its composition. The well was drilled to a depth variously estimated between 1000 and 1300 feet at a point where the surface was approximately 1100 feet above sea-level, consequently the oil pool was probably 200 feet below sea-level. A peculiar method of drilling was necessary in penetrating the wet surface soil and 400 feet of drift sand. When the oil was reached, the four-inch casing weighing 6 tons was driven out with such force that it was sent 200 feet into the air and the column of oil which followed escaped in such quantities that the daily output before the well was capped was estimated at 70,000 barrels.

When received fresh from the well this oil gave a strong odor of hydrogen sulphide. Its specific gravity at 20° was 0.920, corresponding to 22° B., showing it to be heavier than the Corsicana oil, but not so heavy as other specimens of Texas oil examined in this laboratory. It is a high sulphur oil (2.16 per cent.), perhaps the highest in sulphur of any petroleum I have examined. It contains considerable nitrogen, more than 1 per cent. Under atmospheric pressure, it distilled in the following proportions:

	145°–200°.	200°–250°.
Per cent	4	11
Baumé	46°	35°

Under 14 mm. it distilled as follows:

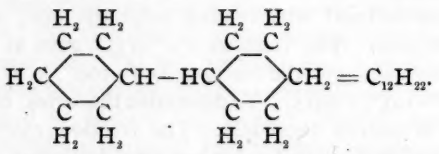
	95°–100°.	150°–200°.	250°–300°.	Residue.
Per cent	17	17	51	15
Baumé	29°	25°	17°	14°

The vacuum distillation was continued until considerable proportions collected at certain temperatures. To determine the series, the distillates 130°–135°, 155°–160°, 190°–195°, were selected for examination. The crude fractions were thoroughly purified with concentrated and with fuming sulphuric acid, and washed with caustic soda. The fraction 130°–135° gave as its specific gravity at 20°, 0.8553, the fraction 155°–160°, 0.8746, and the fraction 190°–195°, 0.8915. To determine the series, combustions were made of each of these oils. The fraction 130°–135° gave 86.86 per cent. carbon, and 13.27 per cent. hydrogen, which corresponds to the symbol $C_{12}H_{22}$, 86.75 per cent. carbon and 13.25 per cent. hydrogen. The molecular weight of this oil at the freezing-point of benzene was found to be 170. The formula $C_{12}H_{22}$ requires 160. The fraction 155°–160° gave 86.26 per cent.

carbon and 13.48 per cent. hydrogen; required for the formula $C_{14}H_{32}$, carbon 86.60 per cent., hydrogen 13.40 per cent. The molecular weight of this fraction at the freezing-point of benzene was found to be 194.1; calculated for $C_{14}H_{26}$, 194. This formula was further confirmed by a determination of the index of refraction which gave 1.473, corresponding to the molecular refraction 62.36; calculated for the formula $C_{16}H_{30}$, 62.33. A combustion of the fraction 190°–195° gave 87.26 per cent. carbon and 12.54 per cent. hydrogen. The formula $C_{16}H_{30}$ requires 87.03 per cent. carbon, 12.97 per cent. hydrogen. The determination of the molecular weight of this fraction at the freezing-point of benzene gave 222.8; calculated for $C_{16}H_{30}$, 222. This formula was also confirmed by the index of refraction which gave 1.484, corresponding to the molecular refraction 71.64; required for the formula $C_{16}H_{30}$, 71.54. The principal hydrocarbons in this petroleum, therefore, are members of the series C_nH_{2n-2}, the same series that Mabery and Buck found in the other petroleum mentioned above, in the lower portions. Since the hydrocarbons in the two oils were fractioned under different pressures, the corresponding differences in temperatures shows an agreement in percentage composition and in molecular weights.

The residue from the last distillation in vacuo gave as its specific gravity 14° Baumé. This oil is, therefore, less rich in the heavier hydrocarbons that make the most valuable lubricators, and asphalts than the heavier Texas oil previously examined.

Since the hydrocarbons in this oil show no evidence of unsaturation, their structure is explained by the assumption of a double methylene ring and its derivatives. Such a structure would correspond to a dihexahydro diphenyl,



The hydrocarbon $C_{14}H_{26}$ should be a dimethyl or an ethyl derivative, and the hydrocarbon $C_{16}H_{30}$ could contain a single butyl side chain, or an equivalent in methyl, ethyl, or propyl side-chains. This homologous series of hydrocarbons presents an interesting field for study, since so little is known about them.

Mr. O. J. Sieplein, instructor, and Mr. A. H. Goldstein, student in this laboratory, have aided in the experimental work on this petroleum. Aid in carrying on this work was received from the C. M. Warren Fund for chemical research.

NOTES.

On Nitrometer Work.—The following work was done on the usual nitrometer, composed of a decomposing bulb and reservoir and the complement of a measuring tube, reduction tube and reservoir. The measuring tube had a capacity of 140 cc. The potassium nitrate used was Merck's, chemically pure, recrystallized. About 0.5 gram was used for each determination. The temperature of the laboratory, while the work was being done, was approximately 68° F. The dry potassium nitrate was weighed out into tared weighing bottles and about 15 cc. of sulphuric acid added. The bottles were then stoppered and set aside for about eighteen hours, or over night, by which time a clear solution was obtained, if the acid used was over 90 per cent. H_2SO_4, but if of less strength a residue, presumably of potassium sulphate, was left. The contents of the weighing-bottles were transferred to the decomposing bulb with the aid of a wash-bottle containing acid of the same strength as that used in the weighing bottles. In each determination 32 cc. of acid were used. The strengths of sulphuric acid used and the volume in cubic centimeters of nitric oxide (NO) per gram of potassium nitrate for each acid are as follows :

Strength of sulphuric acid in per cent.	Cubic centimeters of nitric oxide per gram potassium nitrate.					
	I.	II.	III.	IV.	V.	Average.
98.03	222.0	221.8	222.0	222.3	222.3	222.08
96.92	223.2	223.0	223.3	223.3	....	223.2
96.92	224.0	224.3	224.4	224.4	224.4	224.3
95.14	225.1	224.8	225.0	225.2	225.0	225.0
94.07	225.0	225.0	224.9	225.2	225.0	225.02
93.05	225.1	225.0	224.8	224.9	225.0	224.96
90.90	225.0	224.9	224.9	225.0	225.0	224.96
85.04	225.3	225.1	225.3	225.0	225.3	225.2
80.14	226.2	226.0	226.2	226.2	226.0	226.1

A difference of 4.02 cc. of nitric oxide is thus obtained by the use of the strongest and weakest acids. It seems probable that this is due to the varying absorptive powers for nitric oxide, of the different strengths of sulphuric acid used.

Lunge[1] states that "1 cc. of concentrated vitriol dissolves 0.000593 gram = 0.035 cc. NO." If this 4.02 cc. of nitric oxide per gram, or 2.01 per half gram of potassium nitrate is due to the difference of solubility of nitric oxide in the first and last acids used, then 32 cc. of 98.03 per cent. sulphuric acid absorbs 2.01 cc. nitric oxide and 1 cc. absorbs 0.0628 cc. nitric oxide. For nitrometer work acid of about 95 per cent. H_2SO_4 appears to be the best. Weaker acid attacks the mercury more readily and decomposes nitric acid more slowly. There is no objection to stronger acid except the difficulty of obtaining it. The chemically pure acid made by a well-known company has been found to vary from 95.0 to 98.0 per cent. H_2SO_4.

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NEW BOOKS.

A TEXT-BOOK OF IMPORTANT MINERALS AND ROCKS WITH TABLES FOR THE DETERMINATION OF MINERALS. By S. E. TILLMAN. New York: John Wiley & Sons. 1900. viii + 196 pp. Price, $2.00.

The preface states that the author has designed this book especially for the course in mineralogy at the West Point Military Academy.

The subjects are presented in the order usual in most text-books. Crystallography is treated very briefly: The six systems are defined and illustrated by a few examples. Crystallographic symmetry is defined and contrasted with geometric symmetry. The chemical and physical properties of minerals are reviewed in a short chapter.

Chapter III devotes sixty-four pages to well written descriptions of about seventy-five species, including some well-known gems, ores of the metals, and the common rock-forming minerals.

With the descriptions brief but well selected notes are given as to the occurrence and economic value of many species.

The tables for the determination of minerals are based upon the more obvious physical characteristics and seem well adapted to aid a class in the study of a collection. The book closes with a classification of the common rocks.

The book would seem well adapted for a short practical course in mineralogy if in the hands of a good teacher, otherwise its

[1] *J. Soc. Chem. Ind.*, (1885), p. 447.

abundance of definitions would be out of proportion to its brevity of explanation. N. W. LORD.

ENGINEERING CHEMISTRY. A MANUAL OF QUANTITATIVE CHEMICAL ANALYSIS, FOR THE USE OF STUDENTS, CHEMISTS, AND ENGINEERS. BY THOMAS B. STILLMAN, M.Sc., PH.D., Professor of Analytical Chemistry in the Stevens Institute of Technology. Second edition. With 132 illustrations. Easton, Pa.: The Chemical Publishing Company. 1900. xxii + 503 pp. Price, $4.50.

The first edition of this work was published in 1897, and reviewed in this Journal, in that year (p. 272). In this second edition there has been a transposition of subject-matter so as to bring under one heading, or chapter, the consideration of allied subjects, formerly distributed throughout the volume. The addition of new matter is comparatively small. Some fifteen pages of the first edition have been omitted. One of the valuable characteristics of the work is the number of references to original papers in American, English, German, and French scientific journals. These references have been brought up to date in this edition.

There are some few matters open to criticism. The author only occasionally directs attention to the necessity of repeating separations in gravimetric work, in order to obtain accurate results. In some of his schemes of analysis phosphorus pentoxide is weighed with, and calculated, as alumina. In the analysis of gases by Hempel's apparatus the explosions are made over water, a method Hempel himself has rejected. The table for Baumé's hydrometer for liquids heavier than water, is entirely incorrect.

The work is particularly valuable in that it treats of both the chemical and physical examination of many materials and factory products that are rarely noticed in ordinary laboratory manuals. In comparison with the downpour, we might almost say deluge, of these latter, a manual of this kind is comparatively rare. All that has been said in commendation of the work by the reviewer of the first edition can certainly be endorsed. It is a valuable book. H. PEMBERTON, JR.

A MANUAL OF ASSAYING. BY ALFRED STANLEY MILLER. First edition. New York: John Wiley & Sons. 1900. 91 pp. Price, $1.00.

This little book is to be recommended chiefly for its brevity and clear style. The various methods of fire assaying are so arranged and described as to afford in the minimum space a good, general idea of the subject. It is weak, in common with many

similar works, in sometimes offering impracticable or not strictly correct directions on essential points and in describing methods not equal to those in actual use to-day. In other words, an operator with this book as a basis, would at the outset make but a slow and indifferent workman in an up-to-date assay office. This is, however, to a large extent, simply illustrative of the difference between school instruction and actual competitive practice, and the writer knows of no similar work that presents the subject in a general way more clearly and concisely.

The book is well printed in clear, large type and contains numerous illustrations. ALBERT H. LOW.

A SCHOOL CHEMISTRY, INTENDED FOR USE IN HIGH SCHOOLS AND IN ELEMENTARY CLASSES IN COLLEGES. By JOHN WADDELL. New York: The Macmillan Company. 1900. viii + 278 pp. Price, 90 cents.

The author assumes very properly, that most students fail to obtain clear notions of chemistry from their first course of lectures, or their early struggles with text-book and teacher, but he thinks that the users of this book will fare better than their predecessors. He hopes that the pupil will be able "to discover new facts, to see their connections, * * * to observe the important phenomena, and to understand their full significance." If his hopes should be realized, only partially, what a welcome would be accorded this recent addition to the crowded ranks of elementary text-books!

Five-sixths of the text is allotted to the non-metals, and of the metals only the most common are mentioned. Numerical data are less prominent than in most text-books, even of this class, and only with difficulty can a few problems be discovered. Perhaps the most noticeable features of the book are the clear statement of facts, and the efforts of the author to lead the pupil to observe closely and understandingly. His experience as a teacher and as an examiner, has enabled him to present the subject in a simple and interesting way, and a student who will read this book, make its experiments, and answer conscientiously its interrogations, should acquire a clear, and not insignificant, knowledge of the science and art of chemistry. L. B. HALL.

ELEMENTARY ORGANIC ANALYSIS. FRANCIS GANO BENEDICT. Easton, Pa.: The Chemical Publishing Company. 1900. vi + 86 pp. Price, $1.00.

This manual gives clear and accurate directions for the determination of carbon and hydrogen in organic compounds by com-

bustion in a tube of glass, porcelain, or platinum. After a full discussion of the reagents and apparatus required for the analysis of compounds containing only these elements, the preparation of the tube and the process of combustion are described in an admirable manner. Directions then follow for the combustion of solids containing, besides carbon and hydrogen, nitrogen, the halogens, sulphur or the alkali metals, and also for the analysis of explosive, or difficultly combustible bodies, and liquids. The suggestions which accompany these directions are most valuable, while the numerous references to journals and text-books will be of the greatest assistance when new compounds are to be analyzed.

We believe this book will be helpful to all chemists who may have occasion to carry out the determinations mentioned above, and of still greater value to the student of little experience.

L. B. HALL.

A HANDBOOK OF INDUSTRIAL ORGANIC CHEMISTRY. BY SAMUEL P. SADTLER, PH.D., F.C.S. Third edition. Philadelphia: J. B. Lippincott Co. 1900. 543 pp. Price, $5.00.

Chemists who have had an opportunity to use the earlier editions of Dr. Sadtler's excellent work will welcome most heartily this new edition. It represents more thoroughly than any similar publication the practice of the United States in the organic chemical industries and at the same time covers what is best in the European practice. Full justification is found for the statements of the preface to this edition to the effect that "every chapter has been revised and new matter added. * * * It has been sought to incorporate in this book all of this advance in our knowledge that is definitely acknowledged by chemists. The bibliography has in all chapters been brought down to date and the statistics are the most recent obtainable."

So we find, among other things, new mention and description of the forms of artificial silk, formaldehyde, tanning, dégras, Rohrmann's process for 90 to 100 per cent. acetic acid in one operation. S. B. Boulton's diagram, illustrating the process of distillation of coal, the latter curiously omitted, although mentioned, in the second edition is here introduced.

The matter presented is excellently and logically classified as in the former edition. Raw materials, processes of treatment, products, analytical tests and methods, bibliography and statistics follow each other in the order named. Raw materials and pro-

cesses of treatment are considered fully but in a general way and details often of the utmost importance to the manufacturer are omitted. Yet the information conveyed will be most useful to students and instructors, while the analytical tests and methods and the bibliography and statistics, since they have been brought to date, will be of great value and convenience to the general chemist and in many cases to specialists.

It is to be regretted that some of the later and more widely used forms of machinery have not been included in the illustrations of the book. For instance, in discussion of sugar manufacture the vacuum evaporator of Yaryan is described at some length, while the more widely applicable forms of Wellner-Jelenek and of Swenson are not noticed. The Hepworth centrifugal is figured, but the Weston and the Lafferty forms are not mentioned. In the discussion of recovery coke ovens, the older Appolt and Simon-Carvés' ovens are described and the later Semet-Solvay and Otto-Hoffmann forms, the use of which is so widely extending, both in this country and in Germany, are mentioned only in the table of statistics. Yet it must not be forgotten that in such a volume, devoted to practically the entire field of organic industrial chemistry, space is limited and too much of it cannot be devoted to the various forms of machinery available for the several processes.

Some embarrassing typographical errors, which have carried through the two editions, appear to have escaped the attention of the proof-readers, but they are not such as to be misleading. For instance, only the most inexperienced reader would be misled by the statement that starch "is soluble in cold water, alcohol, ether," etc.

The book is made in the attractive style and finish of the Lippincott Company, is provided with an excellent table of contents, a list of illustrations, and an index, and is to be commended to the favorable consideration of instructors, students, and working chemists.

WM. MCMURTRIE.

COMMERCIAL ORGANIC ANALYSIS. BY ALFRED H. ALLEN, F.I.C., F.C.S. VOL. III. PART I. TANNINS, DYES, AND COLORING-MATTERS, WRITING INKS. Third edition. Revised and edited by J. MERRITT MATTHEWS, Ph.D. Philadelphia: P. Blakiston's Son & Co. 1900. 589 pp. Price, $4.50.

Since the first edition of Mr. Allen's valuable work, its horizon has been considerably enlarged, and the value of the work largely

enhanced. Instead of being strictly a treatise on commercial organic analysis, it has taken on something of the character of a technology. It now treats not only of the tests and methods of estimation of organic substances of commercial value, and of methods for detecting adulterations in them, but it gives in many instances their history, chemical structure, and commercial methods of preparation.

Dr. Matthews has certainly proved himself a worthy successor to Mr. Allen's former collaborator, the late Dr. Leffmann, judging by his work in this volume which includes the tannins, dyes, coloring-matters, and writing inks, all of them subjects with which he is thoroughly familiar, practically as well as theoretically.

The aromatic acids which were in Part I, Vol. III of the second edition, have been transferred to Part III, Vol. II of the third edition, which is in preparation.

The old material has been practically rewritten in bringing it up to date for this volume. The new tannin materials are described, and our best knowledge of tannin analysis, which is far from what it should be, is given in detail. The arrangement of the chapter on dyes and coloring-matters is entirely changed, making decided improvement, and the amount of material is largely increased. Eight pages, at the end of the volume, are devoted to the constitution and analysis of writing inks, and to the chemical examination of ink marks. Almost the whole of this matter is devoted to the iron inks with only a passing mention of the aniline writing fluids. WM. L. DUDLEY.

CHEMICAL TECHNOLOGY OR CHEMISTRY IN ITS APPLICATION TO ARTS AND MANUFACTURES. EDITED BY CHAS. E. GROVES AND WM. THORP. VOL. III. GAS LIGHTING, BY CHAS. HUNT. Philadelphia: P. Blakiston's Son & Co. 1900. xviii+312 pp. Illus. Price, $3.50.

It is eleven years since the publication of the first volume of this work which treated of fuels; and it was six years later that the second volume, on "Lighting by Solid and Liquid Illuminants," made its appearance.

The present volume discusses the manufacture, purification, and distribution of illuminating gas, and its application for lighting purposes, much in the same manner as other works of its kind. The processes and methods refer mainly to English practice.

It is not to be expected that an author can give within the compass of 300 pages, a complete statement of even the present condition of the gas industry and its collateral branches. The present volume, however, might have been considerably enlarged with great advantage, inasmuch as some subjects are treated inadequately or not at all.

Works of this character are, of necessity, largely made up of matter, which in some form has been published or discussed in the technical journals, and we should be much better equipped with such works of reference if there were fewer of them, but if those published treated the subjects in a more exhaustive manner.

The volume will be found of much value on many points connected with the gas industry. It is well printed and liberally illustrated. E. G. LOVE.

A TEXT-BOOK OF CHEMISTRY, INTENDED FOR THE USE OF PHARMACEUTICAL AND MEDICAL STUDENTS. By SAMUEL P. SADTLER, Ph.D., F.C.S., and VIRGIL COBLENTZ, PH.D., F.C.S. In two vols. Philadelphia: J. B. Lippincott Co. 1900.

This is a revised and enlarged edition of the work brought out some years ago by Sadtler and Trimble. Volume I, which is devoted to physics, general and inorganic chemistry, and organic chemistry represents a third edition, while Volume II, on analytical chemistry, is a second edition.

In the presentation of the subject of chemistry to students of medicine and pharmacy it is extremely difficult to select the proper amount as well as the proper kind of information. In earlier attempts in this direction text-books offered to students in these specialties were characterized by a meagerness in detail and inaccuracy in statement which were discouraging to the teacher in search of a suitable manual for class instruction. Even yet we find books designated as "essentials" of chemistry for students of medicine and pharmacy.

But there is now great danger of going too far in the other direction in the production of text-books for these classes of students. The attempt is made to cover a little of everything in the field of chemistry and we have, as a result, treatises quite beyond the needs or capabilities of the embryo drug clerk or physician. If clearness and conciseness of statement are anywhere in order it certainly is in the chemical text-books for such students who are usually beginners, and who, as a rule, suffer

from the defects of irregular preliminary training. A text-book should not be allowed to grow into a large handbook, valuable for reference rather than for every-day study. It is not right that a school text-book to be placed in the hands of boys, beginning the study of chemistry in a college of medicine or pharmacy, should be filled up with the descriptive matters which properly belong in the pharmacopœia, the dispensatories or in a treatise on materia medica, to the exclusion of a clear discussion of the elementary principles of the science, without a knowledge of which, the medical student's notions of chemistry remain forever hazy and unsatisfactory.

The two large volumes before us contain much that is valuable but it appears to the writer that they err in the direction suggested by the last remarks. It is evident that they are written by practical men and on nearly every page of Volume I facts and figures are given which are well to know. Important data concerning hundreds, perhaps thousands, of compounds are included, making of the work a pretty full reference book for most of the isolated facts which the student of medicine or pharmacy is supposed to need at some time. From this standpoint the work is deserving of commendation. But the theoretical treatment is by no means as satisfactory; the student is introduced to a mass of definitions (including a few not very clear paragraphs about ions) before he has learned anything of the preparation or properties of the simpler inorganic substances and compounds, while in the introduction to the subject of organic chemistry we have in the very first pages a discussion of structural formulas, several kinds of isomerism, positive and negative tetrahedra and the difference between maleic and fumaric acids.

There are also a few mistakes in some of these discussions: what is said on page 598 about the optical properties of organic compounds is quite obscure, while the illustrative formula given near the bottom of the page for the calculation of the amount of sugar in a diabetic urine is incorrect. It should be $c = \frac{100 \times 1.5}{52.5 \times l}$. On page 593 "Practical Distillation" is written for what is evidently intended to be "Fractional Distillation."

Volume II contains sections on qualitative analysis, quantitative analysis, pharmaceutical assaying, urine analysis, and the examination of water and milk. This work seems to be fairly

well compiled and will doubtless satisfy the needs of those for whom it is intended. The portion devoted to pharmaceutical assaying would be much improved by including the simple and accurate processes of liquid percolation introduced by Hulsebosch and modified by Schwickerath and others, in which the so-called perforator is used. J. H. LONG.

LABORATORY INSTRUCTIONS IN GENERAL CHEMISTRY. ARRANGED BY ERNEST A. CONGDON. Philadelphia: P. Blakiston's Son & Co. 1901. 110 pp. 8vo. Illus.

The 262 experiments herein described accurately, yet tersely, range from the simplest demonstrations of physical and chemical changes, through the isolation and study of the non-metals (so far as convenient for beginners) up to those dealing with the law of the conservation of matter, the laws of Lavoisier, of Dalton, of Charles, of Boyle, and of Gay-Lussac, and concluding with methods of determining molecular and atomic weights. Throughout the book, the experiments seem to be well graded, carefully chosen, and adequately described; many are elucidated by illustrations of well arranged apparatus.

The material is largely original, and the author has had ten years' experience in testing his exercises as professor in the Drexel Institute, Philadelphia. The present writer would suggest that the introduction sparingly of stoichiometrical examples might strengthen the educational value of this excellent laboratory guide. The book can be used in connection with any standard text-book. Nearly every experiment is followed by queries intended to make the students think for themselves, and the blank pages with which the book is interleaved furnish opportunities for recording replies, as well as the results obtained.

Students pursuing the course herein outlined, will be well prepared to take up the study of qualitative and quantitative analysis. HENRY CARRINGTON BOLTON.

AN INTRODUCTION TO MODERN SCIENTIFIC CHEMISTRY, in the form of popular lectures suited for university extension students and general readers. BY LASSAR-COHN. Translated from the second German edition by M. M. PATTISON-MUIR. New York: D. VanNostrand Company. 1901 348 pp. 12mo. Illus. Price, $2.00.

The plan of this book is well conceived and the subject is skilfully presented; being in the form of popular lectures the style is rather diffuse, though perhaps not more so than necessary for

the comprehension of the class of readers to which the book appeals. The author opens with a discussion of the bearings of physics and of chemistry, and illustrates by describing the distillation of water, and the union of iron with sulphur. We think the definition of chemistry, as given on page 4, rather awkwardly expressed, and liable to the interpretation that it includes, in part, facts that belong to physics.

After making the reader familiar with the practical operations of preparing and examining hydrogen, chlorine, and the other elements of this group, the subjects of atoms and their weights, formulæ, molecules and their weights, and very simple calculations on stoichiometrical principles, are introduced; this postponement of theoretical questions until after certain phenomena have been studied is advantageous. Then follows the study of oxygen, sulphur, and so on. In the chapter on carbon, the student is gently led into the field of organic chemistry, which is exploited only briefly, yet he becomes acquainted with the classification of hydrocarbons, the signification of isomerism and the "chemistry of rings."

In this way, the student insensibly gains some conception of organic chemistry before the term itself is used, and is ready to appreciate the few pages on chemistry of organized substances. Only forty pages are given to metals, and the book closes with an exposition of the periodic law.

A feature of the book is the absence of dogmatic assertions and the continuous introduction of reasoning. Teachers will do well to give the book a trial. The translation bears marks of haste or carelessness. Witness the following phrase: "That apparatus suffices for quite a few purposes only," and the English sentences on several pages. The make-up of the book is excellent; the illustrations are good, and the index is quite full.

HENRY CARRINGTON BOLTON.

FLESH FOODS: THEIR CHEMICAL, MICROSCOPICAL, AND BACTERIOLOGICAL EXAMINATION. BY C. AINSWORTH MITCHELL. London: Charles Griffin & Co., Ltd.; Philadelphia: J. B. Lippincott Co. 1900. xv+336 pp.

This book contains nothing really new or which cannot be found elsewhere in scientific literature, but it has the great merit of containing, in condensed form, methods, investigations, and tables which are scattered here and there in scientific works.

According to the preface, "It has been the author's endeavor to collect and summarize, in a convenient form, records of investi-

gations which are, for the most part, scattered through English and foreign scientific books and periodicals, and to select such methods as appeared most suitable for the examination of meat and its preparations."

Chapters I and II have to do with the structure and chemical composition of muscles, tissues, and blood. In Chapter III, the flesh of animals which are eaten by man, including wild animals, fish, and birds, is described, giving the general characteristics and chemical composition. Next the examination of flesh, both sound and unsound, is taken up, giving methods and chemical constants. The next chapter summarizes some of the ways of preserving flesh, as by salting, drying, smoking, and by use of antiseptics. It includes several tests for antiseptics and preservatives in meat, and the examination of canned goods. One chapter is given to the composition and analysis of sausages, and one to the classification of flesh proteids. The changes due to cooking and the effects of parasites are well described. About thirty pages deal with the bacteriological examination of flesh, describing the principal bacteria which infest flesh, and giving methods for their detection. It closes by giving the best methods for the detection and separation of ptomaines.

The author refers freely to such eminent authorities as König, Chittenden, Hehner, and others.

The attempt has been made to cover such a wide field that it has been necessary to condense the matter much, but the condensation has been done very intelligently.

On the whole, it is a valuable and practical work and will be found a very useful handbook for analytical chemists.

W. B. BROWN.

A TEXT-BOOK OF URINE ANALYSIS FOR STUDENTS AND PRACTITIONERS OF MEDICINE. BY JOHN H. LONG, M.S., Sc.D. Easton, Pa.: The Chemical Publishing Co. 1900. 221 pp. Price, $1.50.

An unusually clear and concise presentation of a well-worn subject. This manual is not only to be recommended to the student of medicine, but equally as well to the chemist and pharmacist, who will find it a great aid in the interpretation of analyses through the numerous references to clinical significance, and the appended tables, which explain in a very lucid manner the relation of pathological conditions to chemical composition. An especially commendable feature is the absence of discussions of

various complicated methods of doubtful value, which crowd many books of this class, much to the confusion of the student. We miss a reference to Howe's modification of Doremus' ureometer, which has added so much to the accuracy and convenience of urea determinations. The illustrations devoted to the microscopical examination of sediments and casts leave room for improvement, both in quality and number. The general make-up of the book is very neat. V. COBLENTZ.

INORGANIC CHEMISTRY. General, Medical and Pharmaceutical, Theoretical and Practical. A text-book and laboratory manual in two volumes. BY OSCAR OLDBERG, PHARM. D. Chicago: Chicago Medical Book Co. 1900. xx + 1177 pp. Price, $7.00.

Volume I is theoretical and descriptive, being divided into three general parts, of which 314 pages are devoted to theoretical chemistry, 150 to the elements and 33 to stoichiometry. Chemical theory is treated in a very thorough and ingenious manner; however, much of this matter could be more readily grasped by the student if classified under the study of the several non-metallic elements. The employment of *approximate* atomic weights, selecting, for example, such values as 120 instead of 120.4 (O = 16) for antimony and 206.5 instead of 206.9 (O = 16) for lead, is not advisable in a text-book of chemistry, for it not only adds to the confusion already existing but also a promiscuous rounding off of these values for convenience sake leads to loose and inaccurate work. The chapter devoted to the periodic system is excellent.

Volume II is more properly a laboratory manual, the first part covering general chemical and pharmaceutical operations, while the second gives working methods for the preparation of 500 pharmaceutical chemicals. No general acknowledgment is made as to the source of the majority of the illustrations.

The work is eminently practical and sufficiently comprehensive to fulfil the requirements of the student and practical pharmacist. The printing and binding is excellent and reflects credit on the publishers. V. COBLENTZ.

HANDBOOK OF PRACTICAL HYGIENE. BY D. H. BERGEY, A.M., M.D. Easton, Pa.: The Chemical Publishing Co. viii + 164 pp. Price, $1.00.

This small work of about 160 pages, to quote the author's preface, is due to "the lack of a convenient handbook for the guidance of students in the sanitary analysis of air, water, soil,

and the principal food materials, and in testing the ventilation of buildings." The author confines himself to the simple methods used in the analysis of the substances mentioned.

The book consists of an introduction, five distinct parts, and a complete index. Part I—Atmospheric Air; Part II—Water; Part III—Soil; Part IV—Sanitary Analysis of Foods; Part V—Ventilation and Heating.

No mention is made of microscopic examinations, of waters, or of food products.

"A Brief Outline of the Sanitary Analysis of Water, Air, etc.," would have been a more appropriate title; the one used is very misleading, as the subject of hygiene is only mentioned in the historical introduction.

The book seems to be intended for the use of the medical student and "may be a means of lightening his labor in this line of study." (?) EDWARD GUDEMAN.

THE CHEMISTS' POCKET MANUAL. BY RICHARD K. MEADE, B.S. Easton, Pa.: The Chemical Publishing Co. 1900. vii+204 pp. Price, $2.00.

This is almost a model work of its kind. Its excellencies are too numerous to mention; among the important ones are good paper, clear type, convenient shape, strong and handsome binding, on the publisher's side, and accuracy, good style, and clearness on the part of the author.

The contents include almost everything which a chemist or metallurgist would consult it for, the data and methods all fresh and up-to-date. Of particular merit are the graphic methods for saving calculation, composition of standard and special reagent solutions, the valuable collection of special methods of technical analysis and the copious references to recent literature.

It being possible to point out but a few of the excellencies of the work, it is almost unfair to indicate its few shortcomings. It is hardly fair to the chemist who buys the book to tell him to recognize a cyanide by pouring hydrochloric acid on it and smelling the gas! (p. 125). Some of the data are intermixed; a little rearrangement would improve the first fifty pages. It should also contain, in my opinion, tables of the heats of combinations of salts, specific heats of compounds, the properties and composition of the most common and useful minerals, and a résumé of assay methods. A marking thread would at times be found

useful. I advise every chemist, metallurgist, and assayer to procure the book.

JOSEPH W. RICHARDS.

ANNUAIRE DE L'OBSERVATOIRE MUNICIPAL DE PARIS, DIT OBSERVATOIRE DE MONTSOURIS, POUR L'ANNÉE 1900. Librairie Gauthier-Villars, Paris. 18mo. 563 pp. Price, 2 francs.

The principal work of this observatory is not star-gazing, but a supervision of the hygiene of the city, as a short perusal of this somewhat belated, but yet valuable, yearly report shows. Founded in 1870, its work is now along the following lines: I. Physical and meteorological, including, besides the usual records, a study of atmospheric electricity, of smoke, of the air of the sewers, etc. II. Chemical, comprising the composition of the air in different parts of the city, in schools, public buildings, sewers; the examination of the water supply, of the Seine water, of the sewer water, and of the subterranean waters in and around Paris; of the rain, snow and fog; also sanitary questions submitted by the municipality, as the efficiency of disinfectants, etc. III. The micrographic service makes bacteriological examinations of the air, water, food, drains, sewage, Seine water, soil, and has a special service for contagious diseases.

The thousands of analyses, conveniently tabulated, will be of great interest and value to all concerned in the sanitation of cities or towns. For example, the carbonic acid in the air at Montsouris, taken every day for fifteen years, averaged 30 liters per 100 cubic meters. It is greater in winter than summer; also greater at night than in daytime at Montsouris, but *vice versa* in Paris.

Altogether, the book is well worth its price, especially to the sanitary chemist. JOSEPH W. RICHARDS.

EXPERIMENTAL PHYSICS. BY EUGENE LOMMEL. Translated by G. W. MYERS from the third German edition. Philadelphia: J. B. Lippincott Co. 1900. xxii + 664 pp.

Eighty-two pages are devoted to motion, 23 to solids, 31 to liquids, 35 to gases, 81 to heat, 17 to magnetism, 56 to electricity, 114 to electrical currents, 47 to waves and sound, 157 to light. This is one of the best text-books on physics that has ever been written, and we have here a very creditable English translation. No book and no translator can hope to avoid all slips and the definition of electromotive force as a quantity of work (p. 334) is

an unfortunate way of putting things, while the spelling of du Bois-Reymond's name on p. 360 and elsewhere must be charged against the translator. Apart from a few similar minor points, the book is phenomenally satisfactory and to be recommended to every one.

WILDER D. BANCROFT.

EVOLUTION OF THE THERMOMETER. By HENRY CARRINGTON BOLTON. Easton, Pa.: The Chemical Publishing Co. 1900. 98 pp. Price, $1.00.

The period covered is the century and a half between 1592 and 1743. The author defends the view that the first thermometer was due to Galileo. This instrument was an air-thermometer with a liquid seal. The plan of measuring the expansion of a liquid in a sealed tube dates from about 1644; in 1664, we find Boyle introducing the idea of a fixed point; in 1669 we have the suggestion of two fixed points by Honoré Fabri; in 1694, Renaldini argued in favor of the freezing-point and boiling-point of water as the two fixed points. The mercury thermometer as a practical instrument is due to Fahrenheit, and for years his instruments were the best in the world. The centesimal scale was suggested by Celsius in 1742; but it will be news to many people that Celsius took the boiling-point of water as zero, and that the inverted scale, which we call by the name of Celsius, was due to Christin. The book is interesting, the illustrations are curious, and the color of the binding is atrocious.

WILDER D. BANCROFT.

THE CHEMICAL ANALYSIS OF IRON. By ANDREW A. BLAIR. Fourth edition. Philadelphia: J. B. Lippincott Co. 1901. xi + 319 pp. Price, $4.00.

The new edition of this standard work on iron analysis has been entirely rewritten and a number of recently improved methods have been incorporated. Among the new material are Vanier's modification of Deshays' method for the rapid determination of manganese in steel, Bamber's method for sulphur in pig-iron, the ether methods for the determination of nickel, chromium, and aluminum and, under carbon, there appear a number of new methods and modifications. The ferro-alloys of molybdenum, chromium, silicon, and titanium are given due attention in this edition. Under coal and coke analysis the methods are those reported by the Committee on Coal Analysis of the American Chemical Society.

P. W. SHIMER.